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A STUDY OF THE PHOTODEGRADATION OF COMMERCIAL DYES

John J. Porter

Clemson University

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A Study of the Photodegradation of Commercial Dyes

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27 Abstract

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This study showed that most commercial colors are resistant to photodegradation and many weeks would be required to produce appreciable dye degradation in a natural aquatic environment. (EPA)

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A STUDY OF THE PHOTODEGRADATION OF COMMERCIAL DYES

By

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Project 12090 EOX

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ABSTRACT

The stability of thirty-six different commercial dyes in water to visible and ultraviolet light from a carbon arc has been studied. The dyes were selected on the basis of their importance in the textile industry from six major classes: basic, acid, direct, vat, disperse and sulfur dyes. A comparison is made for two of the dyes between laboratory fading rates and fading rates in natural sunlight. Both dyes degraded at least 10 times more rapidly in artificial light than in sunlight. Some previously identified degradation products of Basic Green 4 were confirmed, and a mechanism of their formation was proposed. A significant difference in degradation rate was observed between water-soluble dyes and pigment dispersions.

This study showed that most commercial colors are resistant to photodegradation and many weeks would be required to produce appreciable dye degradation in a natural aquatic environment.

This report is submitted in fulfillment of Grant Project No. 12090 EOX between the Environmental Protection Agency and the Department of Textiles, Clemson University.

Key Words: Industrial wastes, textiles, color, dyes, chemical degradation, photodegradation.

CONTENTS

Section		Page
I	Conclusions	1
II	Introduction	3
III	Experimental Results	5
IV	Discussion	33
V	Acknowledgements	91
VI	References	93

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FIGURES

No.		Page
1	Pyrex Cell Used for Dye Degradation Studies	7
2	Structures of Basic Dyes Studied	34
3	Structures of Basic Dyes Studied	35
4	Rate of Photodegradation of Basic Violet 3 in Water at 50°C	36
5	Rate of Photodegradation of Basic Blue 9 in Water at 50°C	37
6	Rate of Photodegradation of Basic Green 1 in Water at 50°C	38
7	Rate of Photodegradation of Basic Green 4 in Water at 50°C	39
8	Rate of Photodegradation of Basic Red 2 in Water at 50°C	40
9	Rate of Photodegradation of Basic Green 4 in Water Exposed to Sunlight and Carbon Arc Light	42
10	Degradation Products Isolated from Basic Green 4	43
11	Mechanism for Degradation of Basic Green 4	44
12	Structures of Acid Dyes Studied	47
13	Structures of Acid Dyes Studied	48
14	Rate of Photodegradation of Acid Red 1 in Water at 50°C	49
15	Rate of Photodegradation of Acid Violet 3 in Water at 50°C	50
16	Rate of Photodegradation of Acid Orange 10 in Water at 50°C	51
17	Rate of Photodegradation of Acid Red 37 in Water at 50°C	52
18	Rate of Photodegradation of Acid Black 52 in Water at 50°C	53
19	Rate of Photodegradation of Acid Violet 43 in Water at 50°C	54
20	Rate of Photodegradation of Acid Blue 40 in Water at 50°C	55
21	Structures of Direct Dyes Studied	57
22	Structures of Direct Dyes Studied	58
23	Rate of Photodegradation of Direct Red 80 in Water at 50°C	59
24	Rate of Photodegradation of Direct Green 6 in Water at 50°C	60
25	Rate of Photodegradation of Direct Black 80 in Water at 50°C	61
26	Rate of Photodegradation of Direct Blue 76 in Water at 50°C	62
27	Rate of Photodegradation of Direct Blue 98 in Water at 50°C	63

FIGURES (continued)

No.		Page
28	Rate of Photodegradation of Direct Red 83 in Water at 50°C	64
29	Rate of Photodegradation of Direct Brown 95 in Water at 50°C	65
30	Rate of Photodegradation of Direct Blue 86 in Water at 50°C	66
31	Rate of Photodegradation of Direct Blue 76 in Water Exposed to Sunlight and Carbon Arc Light	68
32	Structures of Vat Dyes Studied	70
33	Rate of Photodegradation of Vat Brown 3 in Water at 50°C	71
34	Rate of Photodegradation of Vat Violet 1 in Water at 50°C	72
35	Rate of Photodegradation of Vat Blue 6 in Water at 50°C	73
36	Rate of Photodegradation of Vat Green 1 in Water at 50°C	74
37	Structures of Disperse Dyes Studied . . .	76
38	Structures of Disperse Dyes Studied . . .	77
39	Rate of Photodegradation of Disperse Blue 3 in Water at 50°C	78
40	Rate of Photodegradation of Disperse Red 17 in Water at 50°C	79
41	Rate of Photodegradation of Disperse Blue 1 in Water at 50°C	80
42	Rate of Photodegradation of Disperse Blue 27 in Water at 50°C	81
43	Rate of Photodegradation of Disperse Red 60 in Water at 50°C	82
44	Rate of Photodegradation of Disperse Orange 3 in Water at 50°C	83
45	Rate of Photodegradation of Disperse Blue 7 in Water at 50°C	84
46	Rate of Photodegradation of Disperse Red 15 in Water at 50°C	85
47	Rate of Photodegradation of Sulfur Red 5 in Water at 50°C	87
48	Rate of Photodegradation of Sulfur Blue 7 in Water at 50°C	88
49	Rate of Photodegradation of Sulfur Blue 13 in Water at 50°C	89
50	Rate of Photodegradation of Sulfur Black 1 in Water at 50°C	90

TABLES

No.		Page
1	Analyses of Commercial Dyes	8
2	Rate of Photodegradation of Basic Violet 3 in Water at 50°C	11
3	Rate of Photodegradation of Basic Red 2 in Water at 50°C	11
4	Rate of Photodegradation of Basic Blue 9 in Water at 50°C	12
5	Rate of Photodegradation of Basic Green 1 in Water at 50°C	12
6	Rate of Photodegradation of Basic Green 4 in Water at 50°C	13
7	Photodegradation of Basic Green 4 in Water Exposed to Sunlight	13
8	Rate of Photodegradation of Acid Violet 3 in Water at 50°C	14
9	Rate of Photodegradation of Acid Black 52 in Water at 50°C	14
10	Rate of Photodegradation of Acid Orange 10 in Water at 50°C	15
11	Rate of Photodegradation of Acid Violet 43 in Water at 50°C	15
12	Rate of Photodegradation of Acid Red 1 in Water at 50°C	16
13	Rate of Photodegradation of Acid Blue 40 in Water at 50°C	16
14	Rate of Photodegradation of Acid Red 37 in Water at 50°C	17
15	Rate of Photodegradation of Direct Red 80 in Water at 50°C	17
16	Rate of Photodegradation of Direct Blue 86 in Water at 50°C	18
17	Rate of Photodegradation of Direct Brown 95 in Water at 50°C	18
18	Rate of Photodegradation of Direct Blue 76 in Water at 50°C	19
19	Photodegradation of Direct Blue 76 in Water Exposed to Sunlight	19
20	Rate of Photodegradation of Direct Green 6 in Water at 50°C	20
21	Rate of Photodegradation of Direct Blue 98 in Water at 50°C	20
22	Rate of Photodegradation of Direct Red 83 in Water at 50°C	21
23	Rate of Photodegradation of Direct Black 80 in Water at 50°C	21
24	Rate of Photodegradation of Vat Green 1 in Water at 50°C	22
25	Rate of Photodegradation of Vat Blue 6 in Water at 50°C	22

TABLES (continued)

No.		Page
26	Rate of Photodegradation of Vat Violet 1 in Water at 50°C	23
27	Rate of Photodegradation of Vat Brown 3 in Water at 50°C	23
28	Rate of Photodegradation of Disperse Red 17 in Water at 50°C	24
29	Rate of Photodegradation of Disperse Blue 3 in Water at 50°C	24
30	Rate of Photodegradation of Disperse Blue 1 in Water at 50°C	25
31	Rate of Photodegradation of Disperse Orange 3 in Water at 50°C	25
32	Rate of Photodegradation of Disperse Red 15 in Water at 50°C	26
33	Rate of Photodegradation of Disperse Red 60 in Water at 50°C	26
34	Rate of Photodegradation of Disperse Blue 27 in Water at 50°C	27
35	Rate of Photodegradation of Disperse Blue 7 in Water at 50°C	27
36	Rate of Photodegradation of Sulfur Black 1 in Water at 50°C	28
37	Rate of Photodegradation of Sulfur Red 5 in Water at 50°C	28
38	Rate of Photodegradation of Sulfur Blue 7 in Water at 50°C	29
39	Rate of Photodegradation of Sulfur Blue 13 in Water at 50°C	29

SECTION I

CONCLUSIONS

The thirty-six dyes chosen for this study were selected from those most used by the textile industry so that an accurate assessment could be made of the water pollution potential of common commercial colors. The results of the study led to the following conclusions:

1. Most of the dyes are quite resistant to light degradation showing an average of 40 percent color loss after 200 hours exposure to artificial light in water.

2. A comparison of artificial light and natural sunlight effects on Basic Green 4 and Direct Blue 76 showed that these dyes degraded at least 10 times slower in natural sunlight. This means that a minimum of 80 days in a natural environment would be required to produce appreciable degradation of the dyes studied.

3. The water soluble dyes--basic, acid, and direct types--were degraded faster than the insoluble pigment types--vat, disperse and sulfur dyes.

4. The loss of color or degradation of the pigment dispersion type dyes--vat, disperse, and sulfur dyes--appeared to be partly due to physical changes in the dispersion rather than chemical degradation. This is not unusual for these dyes.

5. A mechanism, proposed in previous research work, for the degradation of triphenylmethane type basic dyes was confirmed in this study.

6. The stability of the dyes examined in this study points to the need for color considerations in effluents and stream standards. Waste treatment methods, especially in the textile industry, should be selected for their ability to remove color as well as biodegradable chemicals.

SECTION II

INTRODUCTION

What is the eventual fate of natural and synthetic coloring materials that are discharged into a sewer or industrial waste stream? The total U. S. commercial color production currently amounts to almost 0.5 billion pounds per year.[1] What effect will these colors have on the environment? These questions need qualitative answers at least. Many discharged dyes and pigments are inert and non-toxic at their concentrations in natural receiving waters--some are not so innocuous. In either case, the color they impart may be very undesirable to the water user. This is one of the obvious reasons for research on the stability of dyes to light and water under conditions similar to those encountered when they are discharged to natural streams and reservoirs.

This study is limited to some of the more common dyes used by the textile industry. The total dye consumption of the textile industry is over 100,000,000 pounds per year.[1] Since it has been estimated that a maximum of 90 percent of these dyes end up on fabrics and the remaining 10 percent goes to the waste stream, approximately 10,000,000 pounds of dye per year are presently discharged to waste streams by the textile industry. Some of this color can be removed from the waste by the conventional biological waste treatment systems.[2] The removal occurs when the soluble dye is adsorbed on the sludge or the insoluble dye pigments settle to the bottom of a non-agitated basin or lagoon. Since the dyes are designed to resist oxidative degradation by ozone, bleaches, and oxides of nitrogen it is not likely that the aerobic biological process would have much effect on them. This has been shown in previous research.[3]

A selection of thirty-six dyes for investigation was made from six of the common classes: basic, direct, acid, disperse, vat, and sulfur dyes. The dyes were chosen on the basis of consumptive use so a realistic evaluation of the actual textile waste color problem could be made. Dyes whose structures were not known because of proprietary reasons were not included in the study. The photodegradation in water of the thirty-six dyes, representing many structural types, was investigated. The kinetics of photodegradation were compared to those for sunlight degradation for two of the more fugitive dyes. The difficulty of purification of the dyestuffs and the lack of success in isolating many of the degradation products prevented the determination of quantum yields.

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The decomposition products of the dyes which degraded appreciably were analyzed by mass spectral, gas chromatographic, and infrared methods. Where sufficient information was obtained a mechanism was proposed for the degradation process.

SECTION III

EXPERIMENTAL RESULTS

Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. Gas chromatographic analyses were performed with a Perkin-Elmer Model 900 instrument equipped with a flame ionization detector. Mass spectra were determined by a Hitachi-Perkin-Elmer RMU-7 double focusing mass spectrometer. Ultraviolet spectra were run on a Perkin-Elmer Model 202 spectrophotometer and visible spectra were obtained from a Bausch and Lomb Spectronic 20 spectrophotometer as well as a recording General Electric spectrophotometer. Infrared spectra were run on a Perkin-Elmer Model Infracord.

Fading Rate Studies

The following commercial dyes were used directly from their shipping containers without any prior purification:

C.I. Name	C.I. Number	C.I. Name	C.I. Number
	Basic Dyes		
Basic Green 1	42040	Basic Blue 9	52015
Basic Violet 3	42555	Basic Green 4	42000
Basic Red 2	50240		
	Direct Dyes		
Direct Red 80	35780	Direct Blue 98	23155
Direct Red 83	29225	Direct Blue 76	24410
Direct Black 80	31600	Direct Green 6	30295
Direct Blue 86	74180	Direct Brown 95	30145
	Sulfur Dyes		
Sulfur Black 1	53185	Sulfur Blue 13	53450
Sulfur Blue 7	53440	Sulfur Red 5	53830
	Disperse Dyes		
Disperse Red 15	60710	Disperse Orange 3	11005
Disperse Red 60	*	Disperse Blue 3	61505
Disperse Blue 7	62500	Disperse Red 17	11210
Disperse Blue 27	60767	Disperse Blue 1	64500
	Vat Dyes		
Vat Green 1	59825	Vat Brown 3	69015
Vat Blue 6	69825	Vat Violet 1	60010

*C.I. number not available.

C.I. Name	C.I. Number	C.I. Name	C.I. Number
	Acid Dyes		
Acid Violet 43	60730	Acid Red 1	18050
Acid Blue 40	62125	Acid Red 37	17045
Acid Violet 3	16580	Acid Orange 10	16230
Acid Black 52	15711		

Varied concentrations of the above dyes in aqueous solution were exposed to the carbon arc source of an Atlas Fade-Ometer using a specially constructed cell shown in Figure 1. The cell was designed to accommodate a volume of 800 ml. The side windows were 1/16" Pyrex glass transparent down to 280 mμ at an absorbence of 1.0 (from UV curve). The top of the cell was covered with a glass plate to minimize the evaporation of the liquid but the cell was not sealed so exchange with oxygen in the air could occur. The ambient temperature in the Fade-Ometer cabinet varied from 100-110°F and the temperatures of the dye solutions varied according to the intensity of the coloration of the dye solutions. The glass cell was mounted two inches horizontally from the glass envelope and centered vertically with the carbon arc source. The solutions were exposed to the carbon arc source for a period of 200 hours. The liquid was maintained at its original level throughout the exposure period by frequent additions of distilled water. Little stirring of the dispersions of insoluble dyes was necessary because of convection currents in the warm cell.

The dye concentrations used in this work were based on the elemental analysis of the commercial dye as shown in Table 1, except for sulfur dyes which were based on the dried dye paste and recorded in grams per liter. One milliliter portions of the exposed solutions were taken at approximately 50-hour intervals and analyzed for changes in optical density using a Bausch and Lomb Spectronic 20 spectrophotometer. The results of these experiments are shown in Tables 2-39.

In order to correlate the fading rate of the dye solution in the Fade-Ometer with natural sunlight, two dyes, C.I. Basic Green 4 and C.I. Direct Blue 76, were exposed to sunlight and Fade-Ometer radiation. A 2-liter Pyrex beaker containing 1.5 liters of dye solution was placed on the roof to provide maximum daylight exposure. The top of the beaker was covered with a sheet of the same 1/16" Pyrex glass that was used in construction of the cells. Samples were taken and analyzed in the same manner as for the Fade-Ometer studies.

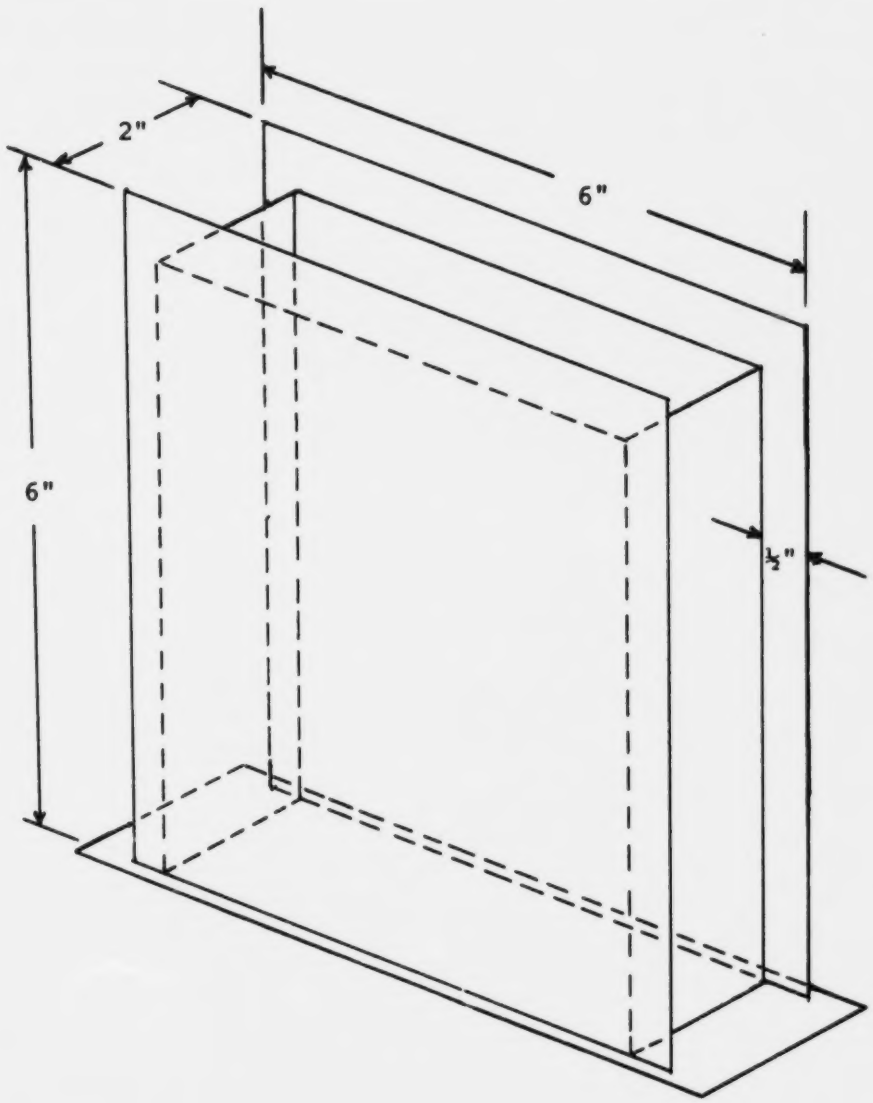

Figure 1 Pyrex Cell Used For Dye Degradation Studies

Table 1 Analyses of Commercial Dyes

C.I. Name	C.I. Number	M.W.	Calculated %C	%H	%N	%S	Found %C	%H	%N	%S	%Active[a]
Basic Green 1	42040	482.0	67.20	7.05	5.81	6.64	65.29	7.16	5.50		97
Basic Violet 3	42555	407.5	73.67	8.72	10.31		70.85	7.70	9.24		90
Basic Red 2	50240	350.5	68.52	5.42	16.03		51.59	6.29	12.36		75
Basic Blue 9	52015	319.5	60.12	5.63	10.01		47.80	4.92	9.98		80
Basic Green 4	42000	926	67.37	5.80	6.04		67.36	6.04	6.04		100
Direct Red 80	35780	134	40.30	1.94	10.40	14.31	11.26	0.99	2.76		26
Direct Red 83	29225	111.1	36.80	1.44	7.60	11.53	9.62	1.24	2.73		27
Direct Black 80	31600	806	53.51	2.78	13.90	7.95	20.82	2.37	8.08		37
Direct Blue 86	74180	781.5	49.40	1.79	14.40	8.19	17.42	1.95	4.75		33
Direct Blue 98	23155	923.0	49.41	2.60	7.59	10.04	12.23	0.90	2.12		28
Direct Blue 76	24410	992.0	41.13	2.42	8.47	12.90	9.91	1.04	2.50		30
Direct Green 6	30295	812.0	50.21	2.71	13.70	7.88	17.40	1.19	4.22		31
Direct Brown 95	30145	759.5	49.00	2.36	11.07	4.22	27.11	1.89	5.19		47
Sulfur Black 1	53185	unknown					40.43	3.38	6.59	18.92	
Sulfur Blue 7	53440	unknown					44.16	4.59	3.43	17.70	
Sulfur Blue 13	53450	unknown					46.30	5.30	2.79	13.19	
Sulfur Red 5	53830	unknown					44.76	4.20	2.35	17.62	

Table 1 (continued)

C.I. Name	C.I. Number	M.W.	Calculated %C	%H	%N	%S	Found %C	%H	%N	%S	%Active[a]
Disperse Red 15	60710	239.0	70.40	3.77	5.86		43.94	3.07	2.44		42
Disperse Red 60		331.0	72.50	3.93	4.23		49.60	3.45	1.30		31
Disperse Blue 7	62500	358	60.35	5.03	7.82		49.47	4.47	3.03		39
Disperse Blue 27	60767	420	62.83	3.81	6.67		37.47	3.39	1.89		28
Disperse Orange 3	11005	242	59.50	4.14	23.15		49.86	4.29	8.36		36
Disperse Blue 3	61505	270	66.7	5.51	10.41		46.62	4.09	3.66		35
Disperse Red 17	11210	344	59.35	5.82	16.29		26.88	2.70	4.44		27
Disperse Blue 1	64500	268	62.70	4.45	20.92	9.15	41.13	3.52	7.33		35
Vat Green 1	59825	516	81.80	3.88			69.04	4.19	Trace		18
Vat Blue 6	69825	513	65.50	2.73	5.46		53.51	4.26	3.27		8
Vat Brown 3	69015	663	76.10	3.17	6.34		59.24	4.93	4.89		43
Vat Violet 1	60010	525	81.25	2.78			54.08	6.24	0.21		15
Acid Violet 43	60730	431	58.49	3.25	3.25	7.43	36.32	2.36	1.93		60
Acid Blue 40	62125	473	55.90	3.48	8.89	6.77	44.22	5.72	2.13		24
Acid Violet 3	16580	483	39.75	2.28	8.70	13.25	25.96	2.70	4.28		49
Acid Black 52	15711	893	42.95	1.79	9.41	7.17	27.65	1.67	3.96		42

Table 1 (continued)

C.I. Name	C.I. Number	M.W.	Calculated %C	Calculated %H	Calculated %N	Calculated %S	Found %C	Found %H	Found %N	Found %S	Found %Active[a]
Acid Red 1	18050	409	52.80	3.18	10.28	15.66	30.88	3.32	7.42		72
Acid Red 37	17045	524	41.21	2.67	10.69	12.21	21.09	2.29	4.85		45
Acid Orange 10	16230	350	54.89	3.14	8.00	9.15	34.45	2.39	5.09		64

[a]Based on the analyses of the commercial dye as received. All dye pastes were dried to constant weight at 105°C before elemental analyses were determined. The limiting element in the analyses was used for %Active calculation for all dyes except sulfur dyes which have no known molecular structure. % Activity for the sulfur dyes was based on the solids obtained after drying the commercial dye paste.

TABLE 2

RATE OF PHOTODEGRADATION OF

BASIC VIOLET 3 IN WATER AT 50°C

Time, Hours	%Transmission[a]	Absorbency[a]	Concentration[b] moles/liter x 10^4
0	30.0	0.520	8.80
56	42.0	0.377	6.38
115	55.6	0.254	4.30
161	67.0	0.172	2.91
200	79.5	0.100	1.69

[a]For Transmission and absorbency measurements a 1 milliliter sample of the dye solution was removed and diluted to 150 milliliters with 95% ethanol. (wavelength = 585mμ)

[b]Based on % activity of commercial dye given in Table 1

TABLE 3

RATE OF PHOTODEGRADATION OF

BASIC RED 2 IN WATER AT 50°C

Time, Hours	%Transmission[a]	Absorbency[a]	Concentration[b] moles/liter x 10^4
0	21.0	0.680	10.75
56	34.8	0.460	7.27
115	43.8	0.360	5.69
161	59.0	0.230	3.63
200	65.3	0.185	2.92

[a]For Transmission and absorbency measurements a 1 milliliter sample of the dye solution was removed and diluted to 150 milliliters with 95% ethanol. (wavelength = 530mμ)

[b]Based on % activity of commercial dye given in Table 1

TABLE 4

RATE OF PHOTODEGRADATION OF

BASIC BLUE 9 IN WATER AT 50°C

Time, Hours	%Transmission[a]	Absorbency[a]	Concentration[b] moles/liter x 10^4
0	20.5	0.690	11.81
56	29.8	0.530	9.07
115	33.7	0.475	8.13
161	39.0	0.410	7.02
200	52.0	0.300	5.13

[a] For Transmission and absorbency measurements a 1 milliliter sample of the dye solution was removed and diluted to 150 milliliters with 95% ethanol. (wavelength = 650m μ)

[b] Based on % activity of commercial dye given in Table 1

TABLE 5

RATE OF PHOTODEGRADATION OF

BASIC GREEN 1 IN WATER AT 50°C

Time, Hours	%Transmission[a]	Absorbency[a]	Concentration[b] moles/liter x 10^4
0	31.0	0.510	9.82
56	40.0	0.400	7.70
115	64.7	0.190	3.66
161	75.5	0.122	2.35
200	88.8	0.051	0.98

[a] For Transmission and absorbency measurements as 1 milliliter sample of the dye solution was removed and diluted to 150 milliliters with 95% ethanol. (wavelength = 637m μ)

[b] Based on % activity of commercial dye given in Table 1

TABLE 6

RATE OF PHOTODEGRADATION OF

BASIC GREEN 4 IN WATER AT 50°C

Time, Hours	%Transmission[a]	Absorbency[a]	Concentration[b] moles/liter x 10^4
0	23.0	0.640	6.38
47	65.5	0.182	1.81
89	72.1	0.139	1.39
200	89.0	0.050	0.50

[a]For Transmission and absorbency measurements a 1 milliliter sample of the dye solution was removed and diluted to 90 milliliters with 95% ethanol. (wavelength = 625 mμ)

[b]Based on % activity of commercial dye given in Table 1

TABLE 7

PHOTODEGRADATION OF BASIC GREEN 4

IN WATER EXPOSED TO SUNLIGHT

Time				Concentration[b]
Days	Hours	%Transmission[a]	Absorbency[a]	moles/liter x 10^4
0	0	25.0	0.600	7.91
13	312	26.0	0.590	7.79
24	576	26.0	0.590	7.79
36	864	29.8	0.530	6.99
42	1008	33.1	0.479	6.32
69	1656	44.0	0.355	4.68

[a]For Transmission and absorbency measurements a 1 milliliter sample of the dye solution was removed and diluted to 120 milliliters with 95% ethanol. (wavelength = 625 mμ)

[b]Based on % activity of commercial dye given in Table 1.

TABLE 8

RATE OF PHOTODEGRADATION OF

ACID VIOLET 3 IN WATER AT 50°C

Time, Hours	%Transmission[a]	Absorbency[a]	Concentration[b] moles/liter x 10^4
0	28.2	0.550	6.29
61	69.0	0.160	1.83
103	84.0	0.075	0.85
156	90.0	0.047	0.53
200	94.0	0.025	0.28

[a]For Transmission and absorbency measurements a 1 milliliter sample of the dye solution was removed and diluted to 40 milliliters with 30% by volume dimethylformamide in distilled water. (wavelength = 705 mμ)

[b]Based on % activity of commercial dye given in Table 1

TABLE 9

RATE OF PHOTODEGRADATION OF

ACID BLACK 52 IN WATER AT 50°C

Time, Hours	%Transmission[a]	Absorbency[a]	Concentration[b] moles/liter x 10^4
0	52.5	0.280	6.65
61	54.0	0.268	6.36
103	53.5	0.270	6.41
156	53.5	0.270	6.41
200	55.0	0.260	6.17

[a]For Transmission and absorbency measurements a 1 milliliter sample of the dye solution was removed and diluted to 40 milliliters with 30% by volume dimethylformamide in distilled water. (wavelength = 650 mμ)

[b]Based on % activity of commercial dye given in Table 1

TABLE 10

RATE OF PHOTODEGRADATION OF

ACID ORANGE 10 IN WATER AT 50°C

Time, Hours	%Transmission[a]	Absorbency[a]	Concentration[b] moles/liter x 10^4
0	27.8	0.560	10.37
61	36.5	0.440	8.15
103	53.7	0.270	5.00
156	94.0	0.025	0.46
200	96.5	0.015	0.28

[a]For Transmission and absorbency measurements a 1 milliliter sample of the dye solution was removed and diluted to 40 milliliters with 30% by volume dimethylformamide in distilled water. (wavelength = 480 mμ)

[b]Based on % activity of commercial dye given in Table 1

TABLE 11

RATE OF PHOTODEGRADATION OF

ACID VIOLET 43 IN WATER AT 50°C

Time, Hours	%Transmission[a]	Absorbency[a]	Concentration[b] moles/liter x 10^4
0	67.5	0.180	8.00
61	73.2	0.130	5.78
103	77.0	0.115	5.11
156	80.5	0.093	4.13
200	83.0	0.080	3.56

[a]For Transmission and absorbency measurements a 1 milliliter sample of the dye solution was removed and diluted to 20 milliliters with 30% by volume dimethylformamide in distilled water. (wavelength = 705 mμ)

[b]Based on % activity of commercial dye given in Table 1

TABLE 12

RATE OF PHOTODEGRADATION OF

ACID RED 1 IN WATER AT 50°C

Time, Hours	%Transmission[a]	Absorbency[a]	Concentration[b] moles/liter x 10^4
0	23.0	0.640	11.37
47	65.5	0.182	10.85
89	72.1	0.139	10.51
200	89.0	0.050	8.18

[a]For Transmission and absorbency measurements a 1 milliliter sample of the dye solution was removed and diluted to 40 milliliters with 30% by volume dimethylformamide in distilled water. (wavelength = 532 mμ)

[b]Based on % activity of commercial dye given in Table 1

TABLE 13

RATE OF PHOTODEGRADATION OF

ACID BLUE 40 IN WATER AT 50°C

Time, Hours	%Transmission[a]	Absorbency[a]	Concentration[b] moles/liter x 10^4
0	55.5	0.255	2.90
47	56.0	0.250	2.85
89	56.5	0.248	2.83
200	60.0	0.223	2.54

[a]For Transmission and absorbency measurements a 1 milliliter sample of the dye solution was removed and diluted to 20 milliliters with 30% by volume dimethylformamide in distilled water. (wavelength = 705 mμ)

[b]Based on % activity of commercial dye given in Table 1

TABLE 14

RATE OF PHOTODEGRADATION OF

ACID RED 37 IN WATER AT 50°C

Time, Hours	%Transmission[a]	Absorbency[a]	Concentration[b] moles/liter x 10^4
0	21.5	0.670	6.56
47	65.5	0.182	1.78
89	89.5	0.047	0.46
200	95.0	0.022	0.22

[a]For Transmission and absorbency measurements a 1 milliliter sample of the dye solution was removed and diluted to 20 milliliters with 30% by volume dimethylformamide in distilled water. (wavelength = 525 mμ)

[b]Based on % activity of commercial dye given in Table 1

TABLE 15

RATE OF PHOTODEGRADATION OF

DIRECT RED 80 IN WATER AT 50°C

Time, Hours	%Transmission[a]	Absorbency[a]	Concentration[b] moles/liter x 10^4
0	23	0.640	2.50
56	23.5	0.630	2.46
111	24.0	0.620	2.42
157	24.5	0.614	2.39
200	26.2	0.580	2.26

[a] For Transmission and absorbency measurements a 1 milliliter sample of the dye solution was removed and diluted to 50 milliliters with 30% by volume dimethylformamide in distilled water. (wavelength = 530 mμ)

[b] Based on % activity of commercial dye given in Table 1

TABLE 16

RATE OF PHOTODEGRADATION OF

DIRECT BLUE 86 IN WATER AT 50°C

Time, Hours	%Transmission[a]	Absorbency[a]	Concentration[b] moles/liter x 10^4
0	23.0	0.640	5.89
56	24.5	0.612	5.63
111	24.0	0.620	5.70
157	26.5	0.580	5.33
200	26.2	0.580	5.33

[a] For Transmission and absorbency measurements a 1 milliliter sample of the dye solution was removed and diluted to 75 milliliters with 30% by volume dimethylformamide in distilled water. (wavelength = 670 mμ)

[b] Based on % activity of commercial dye given in Table 1

TABLE 17

RATE OF PHOTODEGRADATION OF

DIRECT BROWN 95 IN WATER AT 50°C

Time, Hours	%Transmission[a]	Absorbency[a]	Concentration[b] moles/liter x 10^4
0	18.9	0.730	9.77
68	25.0	0.600	8.04
112	29.0	0.540	7.24
154	30.2	0.510	6.82
200	36.0	0.443	5.92

[a] For Transmission and absorbency measurements a 1 milliliter sample of the dye solution was removed and diluted to 100 milliliters with 30% by volume dimethylformamide in distilled water. (wavelength = 470 mμ)

[b] Based on % activity of commercial dye given in Table 1

TABLE 18

RATE OF PHOTODEGRADATION OF

DIRECT BLUE 76 IN WATER AT 50°C

Time, Hours	%Transmission[a]	Absorbency[a]	Concentration[b] moles/liter x 10^4
0	32.8	0.490	3.95
68	73.4	0.133	1.07
112	84.0	0.072	0.58
154	83.0	0.080	0.64
200	89.0	0.050	0.40

[a]For Transmission and absorbency measurements a 1 milliliter sample of the dye solution was removed and diluted to 70 milliliters with 30% by volume dimethylformamide in distilled water (wavelength = 665 mμ)

[b]Based on % activity of commercial dye given in Table 1

TABLE 19

PHOTODEGRADATION OF DIRECT BLUE 76

IN WATER EXPOSED TO SUNLIGHT

Time				
Days	Hours	%Transmission[a]	Absorbency[a]	Concentration[b] moles/liter x 10^4
0	0	62.7	0.205	5.03
13	312	71.0	0.150	3.68
24	576	75.5	0.125	3.07
36	864	76.0	0.120	2.94
42	1008	77.8	0.110	2.70
69	1656	80.1	0.095	2.33

[a]For Transmission and absorbency measurements a 1 milliliter sample of the dye solution was removed and diluted to 100 milliliters with 30% by volume dimethylformamide in distilled water. (wavelength = 665 mμ)

[b]Based on % activity of commercial dye given in Table 1

TABLE 20

RATE OF PHOTODEGRADATION OF

DIRECT GREEN 6 IN WATER AT 50 °C

Time, Hours	%Transmission[a]	Absorbency[a]	Concentration[b] moles/liter x 10^4
0	22.0	0.660	5.54
68	26.0	0.590	4.95
112	29.0	0.540	4.53
154	30.0	0.510	4.28
200	35.0	0.459	3.85

[a]For Transmission and absorbency measurements a 1 milliliter sample of the dye solution was removed and diluted to 70 milliliters with 30% by volume dimethylformamide in distilled water. (wavelength = 650 mμ)

[b]Based on % activity of commercial dye given in Table 1

TABLE 21

RATE OF PHOTODEGRADATION OF

DIRECT BLUE 98 IN WATER AT 50 °C

Time, Hours	%Transmission[a]	Absorbency[a]	Concentration[b] moles/liter x 10^4
0	65.0	0.190	4.01
68	71.8	0.145	3.06
112	73.0	0.137	2.89
154	73.0	0.137	2.89
200	76.7	0.116	2.45

[a]For Transmission and absorbency measurements a 1 milliliter sample of the dye solution was removed and diluted to 70 milliliters with 30% by volume dimethylformamide in distilled water. (wavelength = 650 mμ)

[b]Based on % activity of commercial dye given in Table 1

TABLE 22

RATE OF PHOTODEGRADATION OF

DIRECT RED 83 IN WATER AT 50°C

Time, Hours	%Transmission[a]	Absorbency[a]	Concentration[b] moles/liter x 10^4
0	28.5	0.545	3.11
56	29.8	0.530	3.02
111	34.2	0.464	2.65
157	43.5	0.360	2.05
200	52.8	0.278	1.58

[a] For Transmission and absorbency measurements a 1 milliliter sample of the dye solution was removed and diluted to 50 milliliters with 30% by volume dimethylformamide in distilled water. (wavelength = 537 mμ)

[b] Based on % activity of commercial dye given in Table 1

TABLE 23

RATE OF PHOTODEGRADATION OF

DIRECT BLACK 80 IN WATER AT 50°C

Time, Hours	%Transmission[a]	Absorbency[a]	Concentration[b] moles/liter x 10^4
0	45.0	0.348	6.84
56	47.8	0.320	6.29
111	52.0	0.282	5.54
157	55.0	0.260	5.11
200	57.7	0.240	4.72

[a] For Transmission and absorbency measurements a 1 milliliter sample of the dye solution was removed and diluted to 100 milliliters with 30% by volume dimethylformamide in distilled water. (wavelength = 660 mμ)

[b] Based on %activity of commercial dye given in Table 1

TABLE 24

RATE OF PHOTODEGRADATION OF

VAT GREEN 1 IN WATER AT 50°C

Time, Hours	%Transmission[a]	Absorbency[a]	Concentration[b] moles/liter x 10^4
0	25.0	0.600	4.06
60	27.5	0.560	3.79
110	31.0	0.510	3.46
146	35.7	0.450	3.05
200	43.0	0.367	2.48

[a]For Transmission and absorbency measurements a one milliliter sample of the dye solution was removed and diluted to 20 milliliters with dimethylformamide. (wavelength = 660 mμ)

[b]Based on % activity of commercial dye given in Table 1

TABLE 25

RATE OF PHOTODEGRADATION OF

VAT BLUE 6 IN WATER AT 50°C

Time, Hours	%Transmission[a]	Absorbency[a]	Concentration[b] moles/liter x 10^4
0	71.0	0.150	1.91
60	72.5	0.140	1.79
110	76.0	0.120	1.53
146	77.8	0.110	1.44
200	82.0	0.086	1.10

[a]For Transmission and absorbency measurements a one milliliter sample of the dye solution was removed and diluted to 20 milliliters with dimethylformamide. (wavelength = 695 mμ)

[b]Based on % activity of commercial dye given in Table 1

TABLE 26

RATE OF PHOTODEGRADATION OF

VAT VIOLET 1 IN WATER AT 50°C

Time, Hours	%Transmission[a]	Absorbency[a]	Concentration[b] moles/liter x 10^4
0	41.0	0.390	4.20
60	44.0	0.353	3.81
110	49.0	0.310	3.34
146	52.2	0.280	3.02
200	58.0	0.237	2.55

[a]For Transmission and absorbency measurements a one milliliter sample of the dye solution was removed and diluted to 20 milliliters with dimethylformamide. (wavelength = 550 mμ)

[b]Based on % activity of commercial dye given in Table 1

TABLE 27

RATE OF PHOTODEGRADATION OF

VAT BROWN 3 IN WATER AT 50°C

Time, Hours	%Transmission[a]	Absorbency[a]	Concentration[b] moles/liter x 10^4
0	29.5	0.530	9.33
60	32.3	0.490	8.62
110	37.5	0.425	7.48
146	41.0	0.388	6.82
200	49.0	0.310	5.46

[a]For Transmission and absorbency measurements a one milliliter sample of the dye solution was removed and diluted to 20 milliliters with dimethylformamide. (wavelength = 550 mμ)

[b]Based on % activity of commercial dye given in Table 1

TABLE 28

RATE OF PHOTODEGRADATION OF

DISPERSE RED 17 IN WATER AT 50°C

Time, Hours	%Transmission[a]	Absorbency[a]	Concentration[b] moles/liter x 10^4
0	28.5	0.545	10.29
70	33.0	0.480	9.06
103	34.0	0.465	8.78
157	37.8	0.423	7.98
200	41.8	0.380	7.17

[a]For Transmission and absorbency measurements a one milliliter sample of the dye solution was removed and diluted to 70 milliliters with dimethylformamide. (wavelength = 505 mμ)

[b]Based on % activity of commercial dye given in Table 1

TABLE 29

RATE OF PHOTODEGRADATION OF

DISPERSE BLUE 3 IN WATER AT 50°C

Time, Hours	%Transmission[a]	Absorbency[a]	Concentration[b] moles/liter x 10^4
0	47.5	0.320	3.59
70	56.0	0.251	2.82
103	60.5	0.220	2.47
157	67.0	0.173	1.94
200	74.0	0.130	1.46

[a]For Transmission and absorbency measurements a one milliliter sample of the dye solution was removed and diluted to 70 milliliters with dimethylformamide. (wavelength = 650 mμ)

[b]Based on % activity of commercial dye given in Table 1

TABLE 30

RATE OF PHOTODEGRADATION OF

DISPERSE BLUE 1 IN WATER AT 50°C

Time, Hours	%Transmission[a]	Absorbency[a]	Concentration[b] moles/liter x 10^4
0	26.3	0.580	19.45
70	34.8	0.460	15.42
103	39.0	0.410	13.75
157	41.0	0.388	13.01
200	39.0	0.410	13.75

[a]For Transmission and absorbency measurements a one milliliter sample of the dye solution was removed and diluted to 70 milliliters with dimethylformamide. (wavelength = 650 mμ)

[b]Based on % activity of commercial dye given in Table 1

TABLE 31

RATE OF PHOTODEGRADATION OF

DISPERSE ORANGE 3 IN WATER AT 50°C

Time, Hours	%Transmission[a]	Absorbency[a]	Concentration[b] moles/liter x 10^4
0	21.0	0.680	22.53
70	22.0	0.660	21.87
103	23.0	0.640	21.20
157	24.1	0.620	20.54
200	23.5	0.630	20.87

[a]For Transmission and absorbency measurements a one milliliter sample of the dye solution was removed and diluted to 100 milliliters with dimethylformamide. (wavelength = 445 mμ)

[b]Based on % activity of commercial dye given in Table 1

TABLE 32

RATE OF PHOTODEGRADATION OF

DISPERSE RED 15 IN WATER AT 50°C

Time, Hours	%Transmission[a]	Absorbency[a]	Concentration[b] moles/liter x 10^4
0	23.8	0.624	24.71
60	26.0	0.590	23.36
105	25.8	0.595	23.56
151	27.5	0.560	22.18
200	26.2	0.580	22.97

[a]For Transmission and absorbency measurements a one milliliter sample of the dye solution was removed and diluted to 70 milliliters with dimethylformamide. (wavelength = 537 mμ)

[b]Based on % activity of commercial dye given in Table 1

TABLE 33

RATE OF PHOTODEGRADATION OF

DISPERSE RED 60 IN WATER AT 50°C

Time, Hours	%Transmission[a]	Absorbency[a]	Concentration[b] moles/liter x 10^4
0	40.0	0.400	12.16
60	42.3	0.370	11.25
105	43.6	0.360	10.94
151	45.3	0.341	10.36
200	44.8	0.346	10.52

[a]For Transmission and absorbency measurements a 1 milliliter sample of the dye solution was removed and diluted to 70 milliliters with dimethylformamide. (wavelength = 555 mμ)

[b]Based on % activity of commercial dye given in Table 1

TABLE 34

RATE OF PHOTODEGRADATION OF

DISPERSE BLUE 27 IN WATER AT 50°C

Time, Hours	%Transmission[a]	Absorbency[a]	Concentration[b] moles/liter x 10^4
0	38.0	0.420	10.71
60	36.2	0.440	11.22
105	35.6	0.450	11.47
151	37.5	0.428	10.91
200	36.0	0.441	11.24

[a]For Transmission and absorbency measurements a 1 milliliter sample of the dye solution was removed and diluted to 20 milliliters with dimethylformamide. (wavelength = 537 mμ)

[b]Based on % activity of commercial dye given in Table 1

TABLE 35

RATE OF PHOTODEGRADATION OF

DISPERSE BLUE 7 IN WATER AT 50°C

Time, Hours	%Transmission[a]	Absorbency[a]	Concentration[b] moles/liter x 10^4
0	24.2	0.616	16.06
60	26.8	0.580	15.12
105	28.0	0.550	14.34
151	30.1	0.520	13.55
200	31.5	0.500	13.03

[a]For Transmission and absorbency measurements a 1 milliliter sample of the dye solution was removed and diluted to 50 milliliters with dimethylformamide. (wavelength = 650 mμ)

[b]Based on % activity of commercial dye given in Table 1

TABLE 36

RATE OF PHOTODEGRADATION OF

SULFUR BLACK 1 IN WATER AT 50°C

Time, Hours	%Transmission[a]	Absorbency[a]	Concentration[b] grams/liter
0	57.8	0.240	1.92
70	63.0	0.200	1.60
159	65.0	0.190	1.52
200	67.3	0.175	1.40

[a]For Transmission and absorbency measurements a 2 milliliter sample of the dye solution was diluted to twenty milliliters with a solution containing 5% $Na_2S_2O_4$ and 3% NaOH. (wavelength = 400 mμ)

[b]Based on the analyses of the commercial dye paste for total solids.

TABLE 37

RATE OF PHOTODEGRADATION OF

SULFUR RED 5 IN WATER AT 50°C

Time, Hours	%Transmission[a]	Absorbency[a]	Concentration[b] grams/liter
0	32.3	0.490	1.98
70	34.5	0.460	1.86
159	39.0	0.410	1.65
200	40.0	0.400	1.61

[a]For Transmission and absorbency measurements a 2 milliliter sample of the dye solution was diluted to twenty milliliters with a solution containing 5% $Na_2S_2O_4$ and 3% NaOH. (wavelength = 400 mμ)

[b]Based on the analyses of the commercial dye paste for total solids.

TABLE 38

RATE OF PHOTODEGRADATION OF

SULFUR BLUE 7 IN WATER AT 50°C

Time, Hours	%Transmission[a]	Absorbency[a]	Concentration[b] grams/liter
0	22.0	0.660	2.16
70	24.8	0.610	2.00
159	23.0	0.640	2.10
200	25.0	0.600	1.96

[a]Transmission and absorbency measurements a 2 milliliter sample of the dye solution was diluted to twenty milliliters for a solution containing 5% $Na_2S_2O_4$ and 3% NaOH. (wavelength = 400 mμ)

[b]Based on the analyses of the commercial dye paste for total solids.

TABLE 39

RATE OF PHOTODEGRADATION OF

SULFUR BLUE 13 IN WATER AT 50°C

Time, Hours	%Transmission[a]	Absorbency[a]	Concentration[b] grams/liter
0	52.2	0.280	1.27
70	54.8	0.260	1.18
159	54.8	0.260	1.18
200	60.5	0.220	1.08

[a]For Transmission and absorbency measurements a 2 milliliter sample of the dye solution was diluted to twenty milliliters with a solution containing 5% $Na_2S_2O_4$ and 3% NaOH. (wavelength = 400 mμ)

[b]Based on the analyses of the commercial dye paste for total solids.

The following dyes showed greater than 50% loss in optical density after 200 hours Fade-Ometer radiation and were analyzed for identification of degradation products:

Basic Green 1	C.I. 42040	Direct Red 83	C.I. 29225
Basic Red 2	C.I. 50240	Direct Blue 76	C.I. 24410
Basic Violet 3	C.I. 42555	Vat Blue 6	C.I. 69825
Basic Green 4	C.I. 42000	Acid Red 37	C.I. 17045
Basic Blue 9	C.I. 50215	Acid Orange 10	C.I. 16230
Disperse Blue 3	C.I. 61505	Acid Violet 3	C.I. 16580

At the completion of the exposure period, the faded samples were removed from the cells, placed in polyethylene bottles and stored at -20°C in a freezer to prevent further reactions which may have been initiated in the Fade-Ometer.

The samples were removed several times from the freezer, allowed to thaw and immediately replaced in the freezer. This was done to separate decomposition products from the aqueous solution without promoting further decomposition.

After this approximately 250 ml of the faded solution was filtered in a gravity funnel. The collected precipitate was allowed to air dry and then rinsed from the filter paper with spectro grade acetone.

For those dyes from which no precipitate was collected, the water solution of the dye was placed on a watch glass and allowed to evaporate at room temperature. The samples were covered to prevent atmospheric contamination.

Solid residues isolated by both methods were analyzed by mass spectrometry using the solids probe or gas-chromatograph inlet system, and by gas chromatography when volatile residues were obtained.

The conditions generally used for the gas chromatograph were:

Helium Flow	30 ml/min
Injection Port Temp.	325°C
Column Temp.	100-275°C (Isothermal at 275°)
Manifold Temp.	320°C

Column: 1/8", 6 foot stainless steel, SE 30 silicone oil

Chemical Preparations

The leuco carbinol forms of Basic Green 1, Basic Green 4, and Basic Violet 3 were prepared to provide knowns for degradation product identification.

To approximately 3 grams of commercial dye in 100 ml of distilled water, 5 ml of concentrated ammonium hydroxide was added. The resulting precipitate was filtered, washed and dried. After drying, the residue was dissolved in benzene to remove inorganic impurities, filtered and the benzene evaporated. The isolated crystals were used as knowns.

Other reference compounds were purchased from commercial suppliers.

SECTION IV

DISCUSSION

Commercial dyes may be considered to be either relatively inert or unstable. To most the term inert would describe stable behavior upon exposure to near-ultraviolet and visible light. However, since most dyes are applied to fibers from aqueous solution, the part that water plays in the degradation process cannot be neglected. All results reported in this study were obtained from water solutions or suspensions. The data, therefore, reflect the combined effects of light and water. The basic dyes showed the most degradation and will be the first class discussed.

Basic Dyes

Basic dyes are cationic organic molecules capable of dyeing wool, polyester, acrylic and other fibers that have been prepared to contain anionic sites which attract and interact with cationic molecules.[4] These dyes were first discovered in 1859 by Verguin[5] in France and some of the original dyes are still in use.

These dyes are applied from an aqueous solution containing enough acetic acid to adjust the pH to 4-6. The weight of the dyebath will generally be 20 times the weight of fabric being dyed. The solution is carefully heated to 190°F and held there for one to two hours. The bath is then cooled, discharged and fresh water added to rinse surface dye from the fibers.

Basic dyes are the brightest class of soluble dyes used by the textile industry. Their tinctorial value is very high causing less than 1 ppm of the dye to produce an obvious water coloration. This factor would cause these dyes to have the greatest potential threat of coloration to a natural water supply. Fortunately these dyes are adsorbed by many minerals and organic matter so natural processes can generally remove them from a stream without the help of sunlight if given sufficient time.

The structures of the basic dyes used in this study are shown in Figures 2 and 3. These structures represent the triphenylmethane, phenazine and thiazine types.

The fading rate curves for the basic dyes are shown in Figures 4 to 8. The basic dyes all showed appreciable degradation during their 200-hour exposure to visible and ultraviolet light. To compare the effect of sunlight and artificial light Basic Green 4 was exposed

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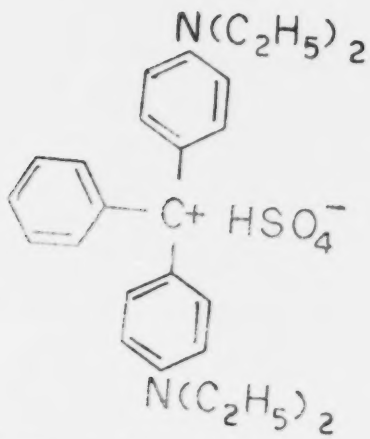
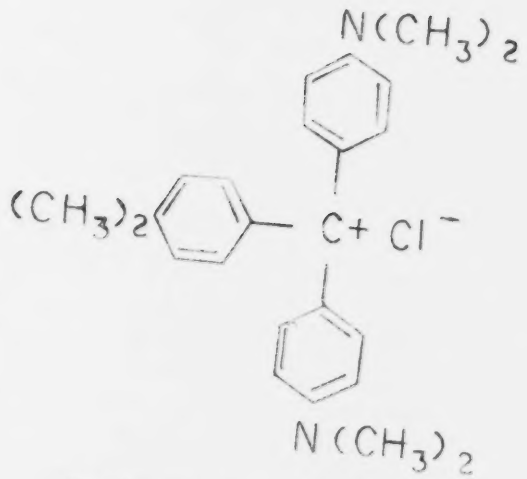


Basic Green 1 C.I. 42040



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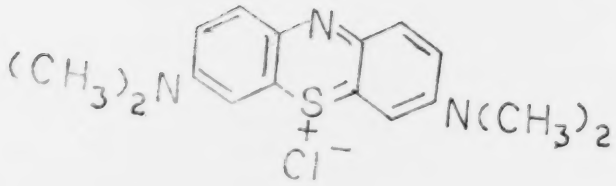
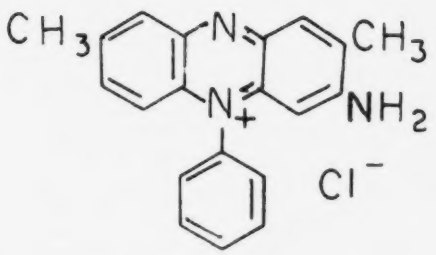
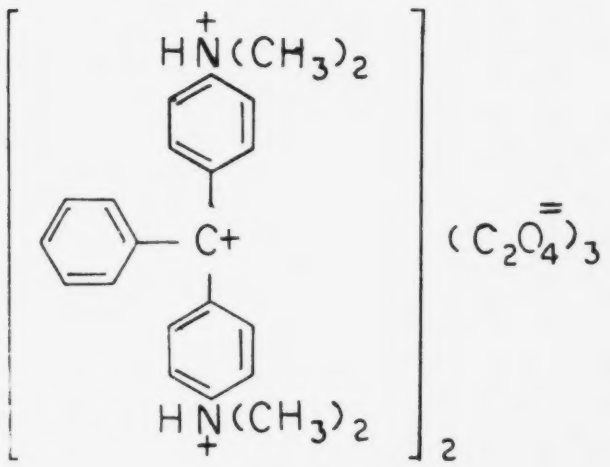


Basic Red 2 C.I. 50240

Figure 2 Structures of Basic Dyes Studied



Basic Blue 9 C. I. 52015



Basic Green 4 C.I. 42000

Figure 3 Structures of Basic Dyes Studied

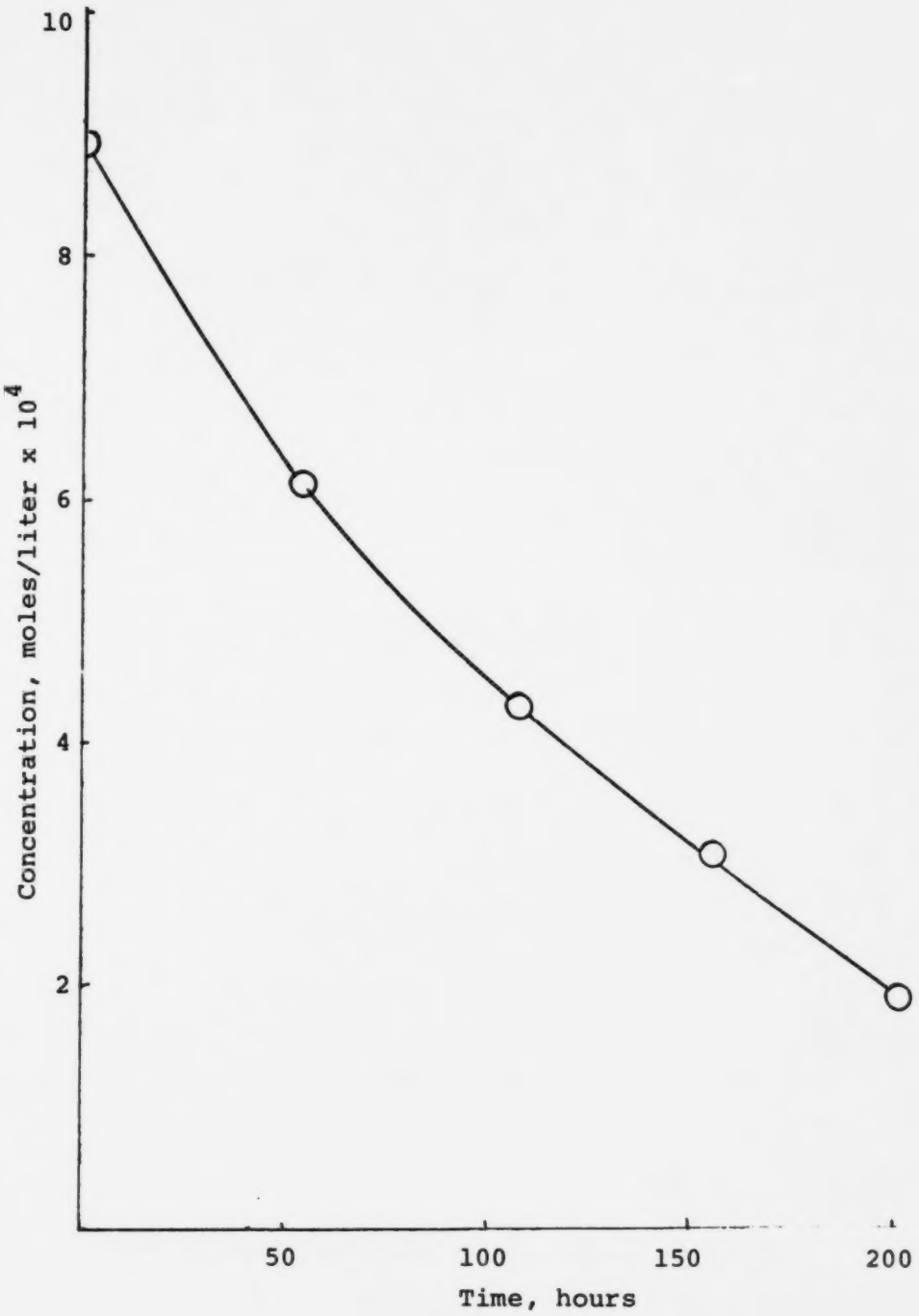


Figure 4 Rate of Photodegradation of Basic Violet 3 in Water at 50°C.

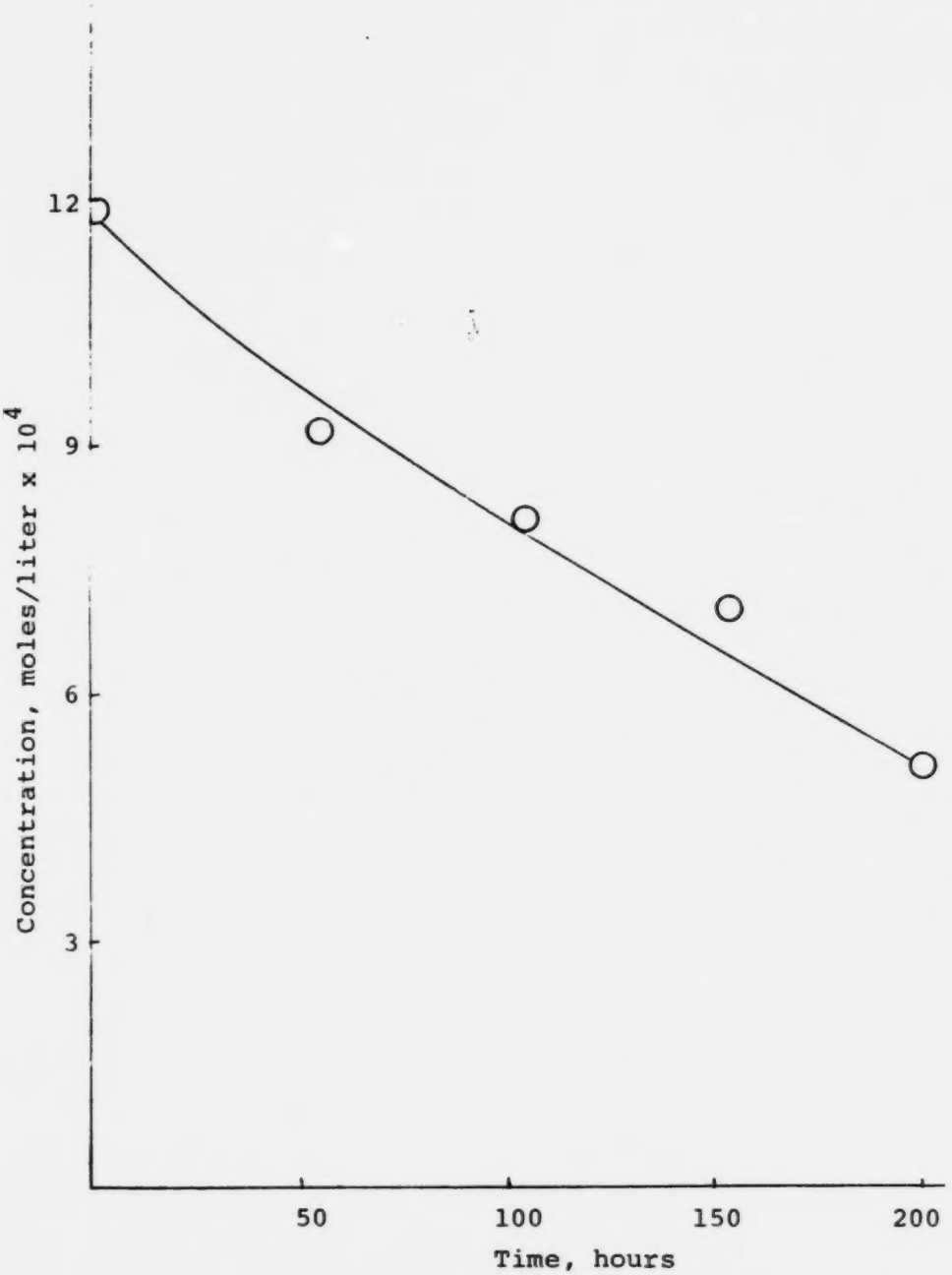


Figure 5 Rate of Photodegradation of Basic Blue 9 in Water at 50°C.

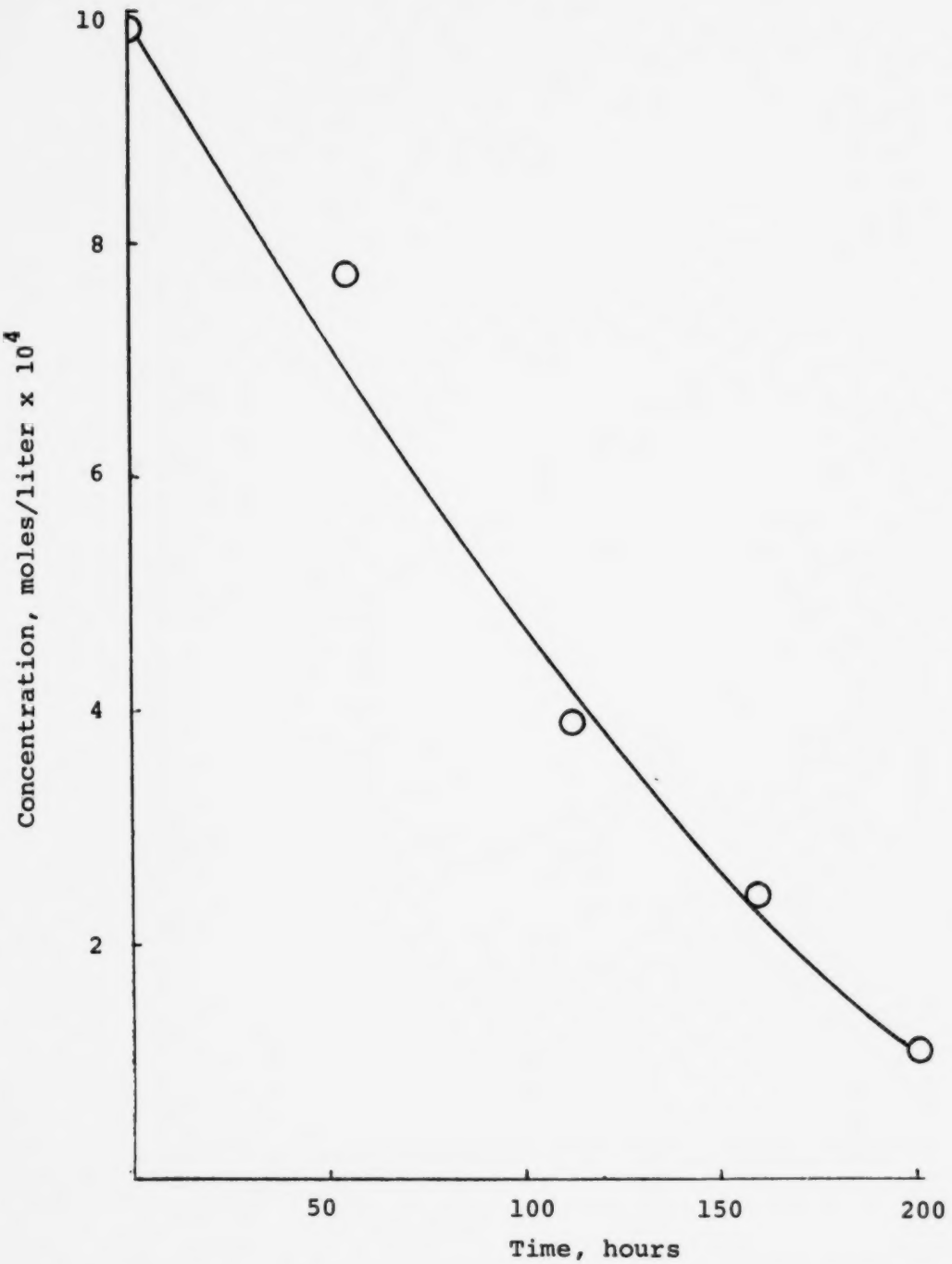


Figure 6 Rate of Photodegradation of Basic Green 1 in Water at 50°C.

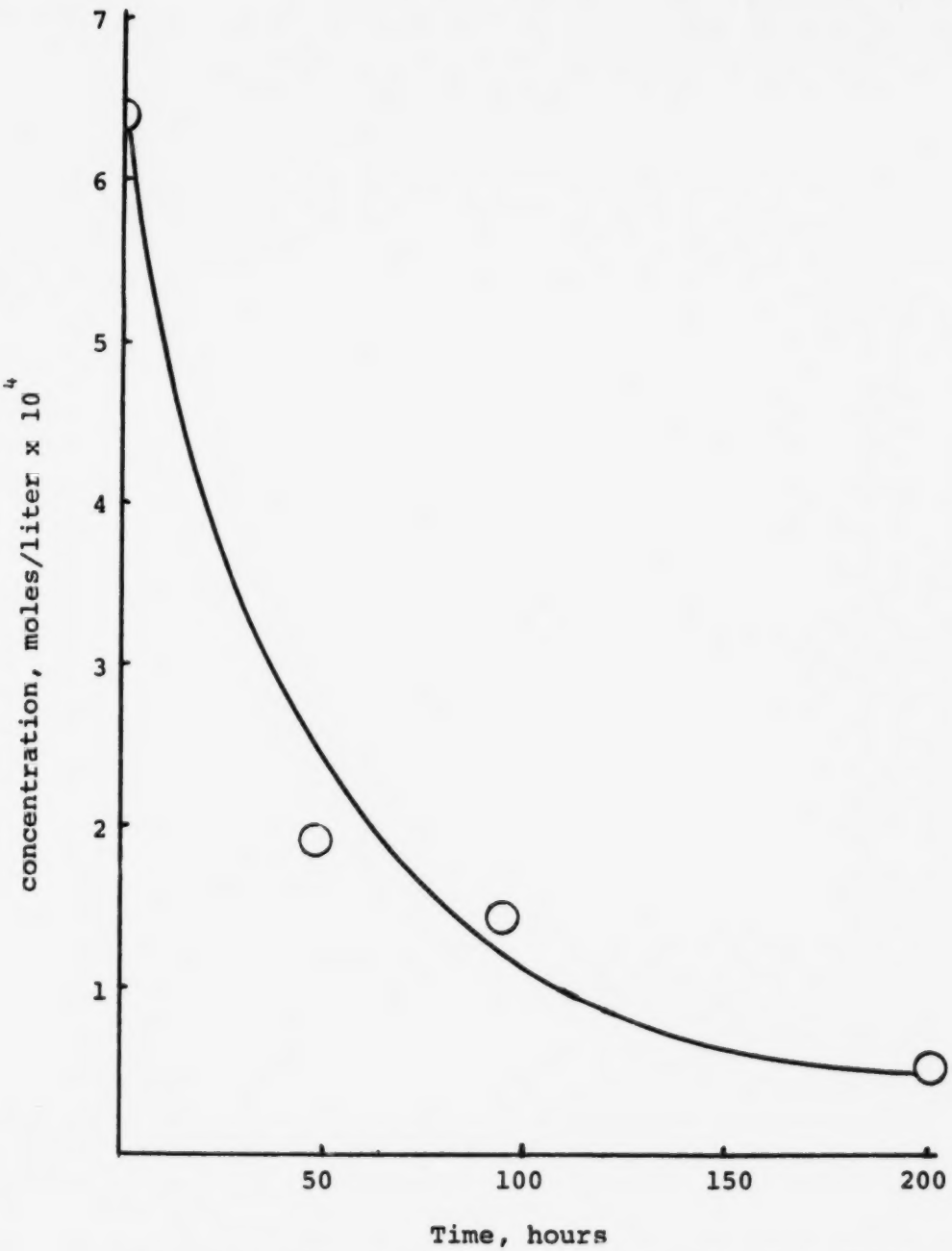


Figure 7 Rate of Photodegradation of Basic Green 4 in Water at 50°C.

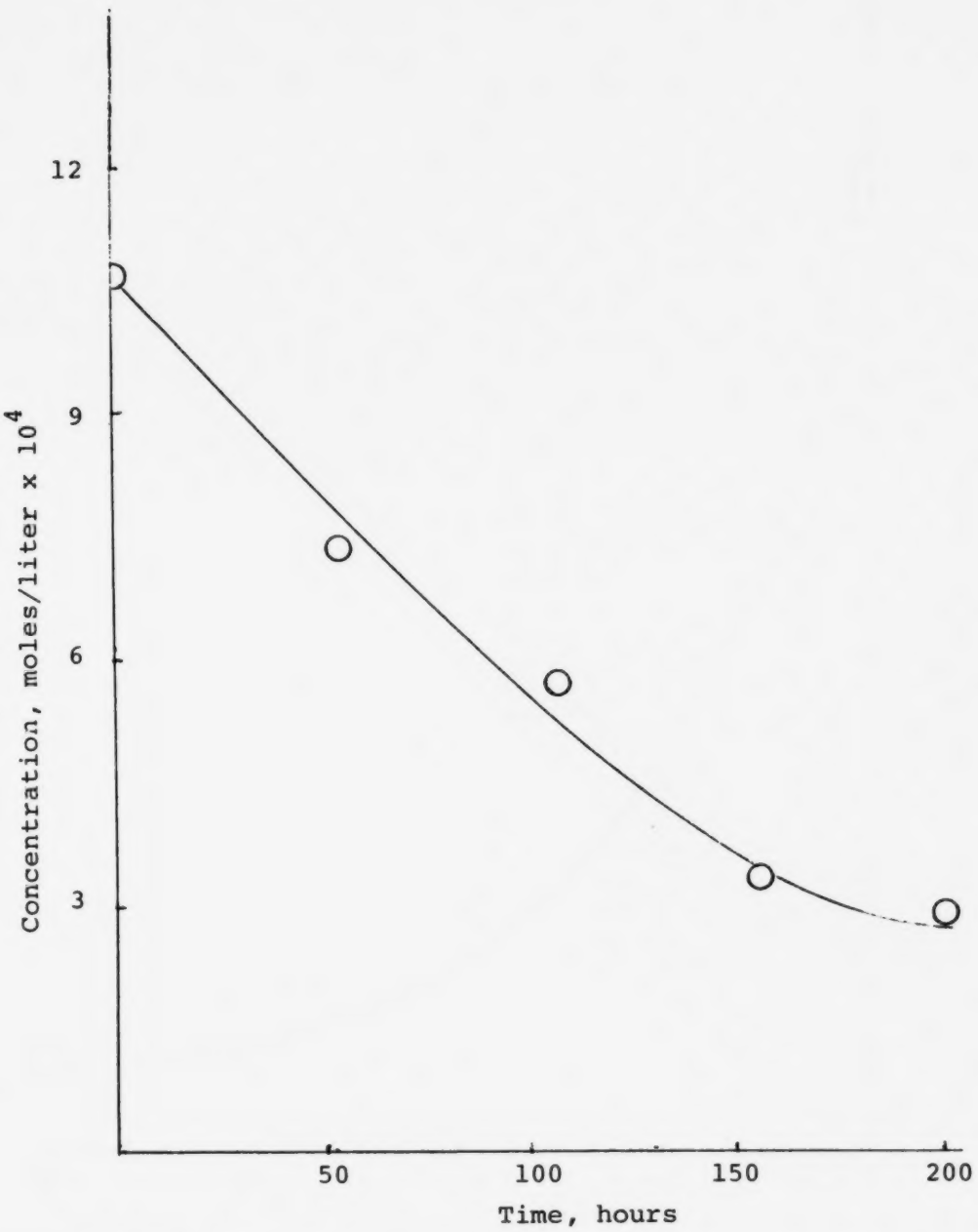


Figure 8 Rate of Photodegradation of Basic Red 2 in Water at 50°C.

to sunlight on the roof of the building. The degradation rate curve for natural light is shown in Figure 9 with the data from Figure 7 plotted on this figure for comparison. The fading rate in artificial light is much faster as expected--the data indicate that the fading rate is at least 10 times as fast. This check was repeated with one of the direct dyes and is reported later.

The degradation products that could be identified by mass spectrometry and gas chromatography from Basic Green 4 are shown in Figure 10. The products isolated show some correlation with data obtained previously by other researchers.[6] The results of this study and other studies[7] show that these dyes may decompose by two principal paths. A proposed mechanism for the degradation of the triphenylmethane dyes is shown in Figure 11.

The carbinol form of the dye is converted to the excited state (possibly triplet) by absorption of ultraviolet light. The excited molecule is converted into products by: (1) fragmentation into radicals and rapid reaction of the radical moieties with oxygen and water to give the products isolated, or (2) concerted reaction of the excited carbinol form with oxygen and water to give degradation products directly. Oxygen seems to be necessary for the formation of the products obtained, which is in agreement with the results of previous studies.[6]

Evidence for the degradation of the carbinol form and not the cation is seen in the work reported by Bitzer and Brielmaier.[7] They found the rate of decomposition to be inversely proportional to the hydrogen ion concentration in a pH range between 1 and 5.

By adding phloroacetophenone to an alcohol solution of CI Basic Green 4, Bitzer[7] found that the time required for bleaching the solution was increased from two days to several weeks. He attributed this to the fact that the adsorption region of the ketone and the dye were similar, so both compounds would be absorbing the same degradative radiation.[8]

Most covalent bonds have dissociation energies which are well within the energy range of natural and artificial daylight. The enclosed carbon arc light source produces a spectral wavelength range of 279 nm to 12,000 nm[9] which corresponds to energies of 95.3 to 40.9 kcal/mole, respectively. Since most dyes have adsorption maxima within this region, it is understandable that a number of them are vulnerable to photochemical degradation.

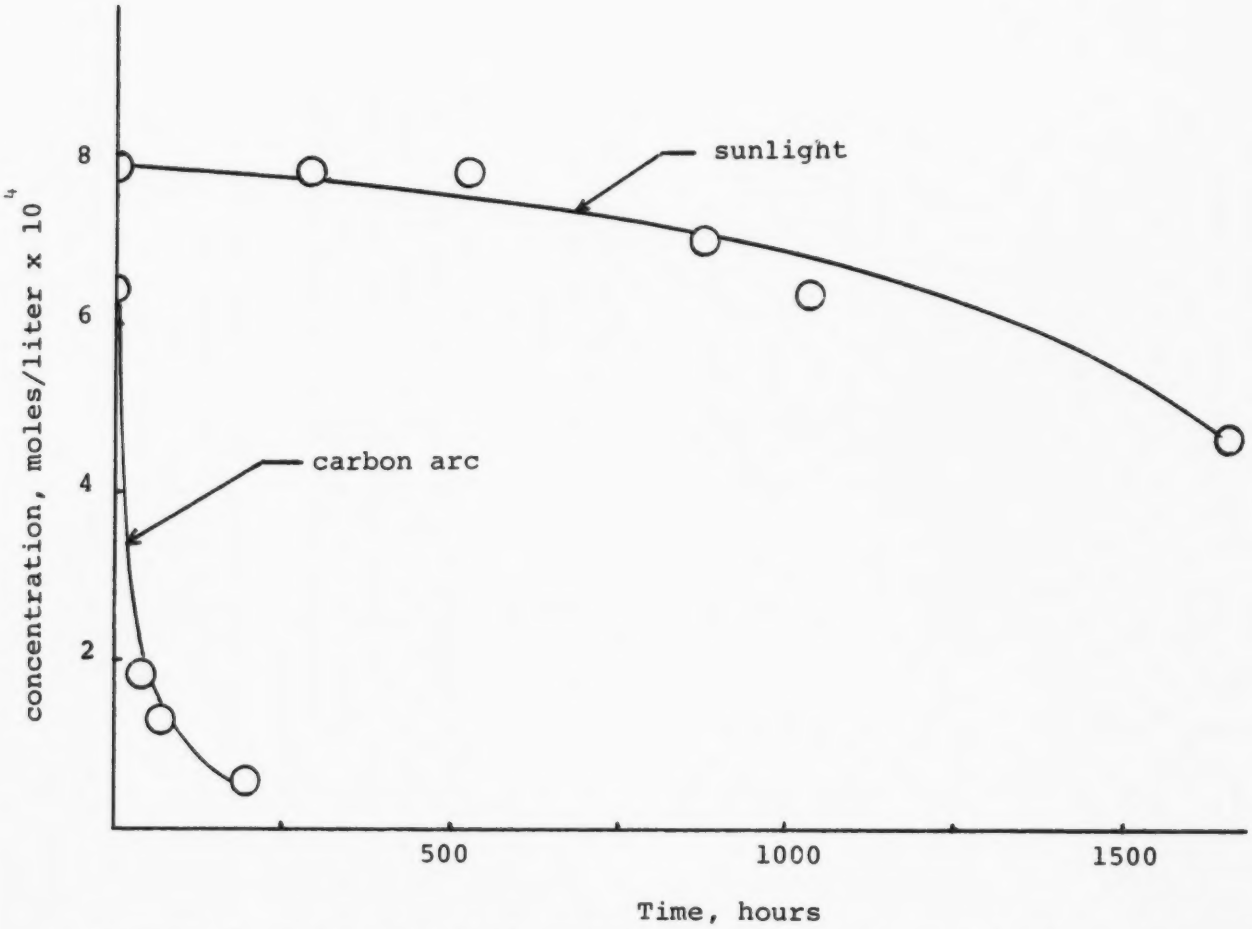
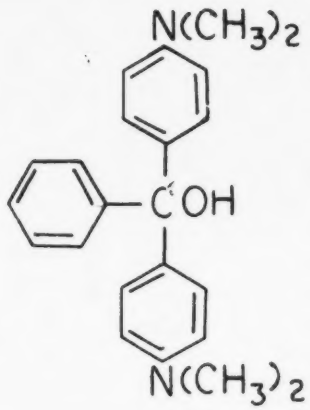
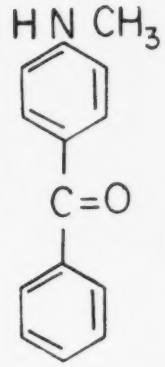


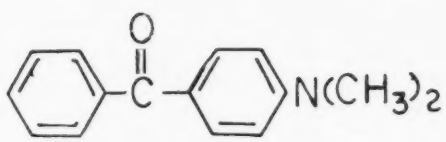
Figure 9 Rate of Photodegradation of Basic Green 4 in Water Exposed to Sunlight and Carbon Arc Light



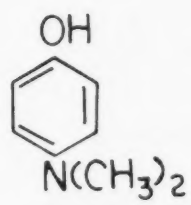
Leuco base



p-Methylaminobenzophenone



p-Dimethylaminobenzophenone



p-Dimethylaminophenol

Figure 10 Degradation Products Isolated from Basic Green 4

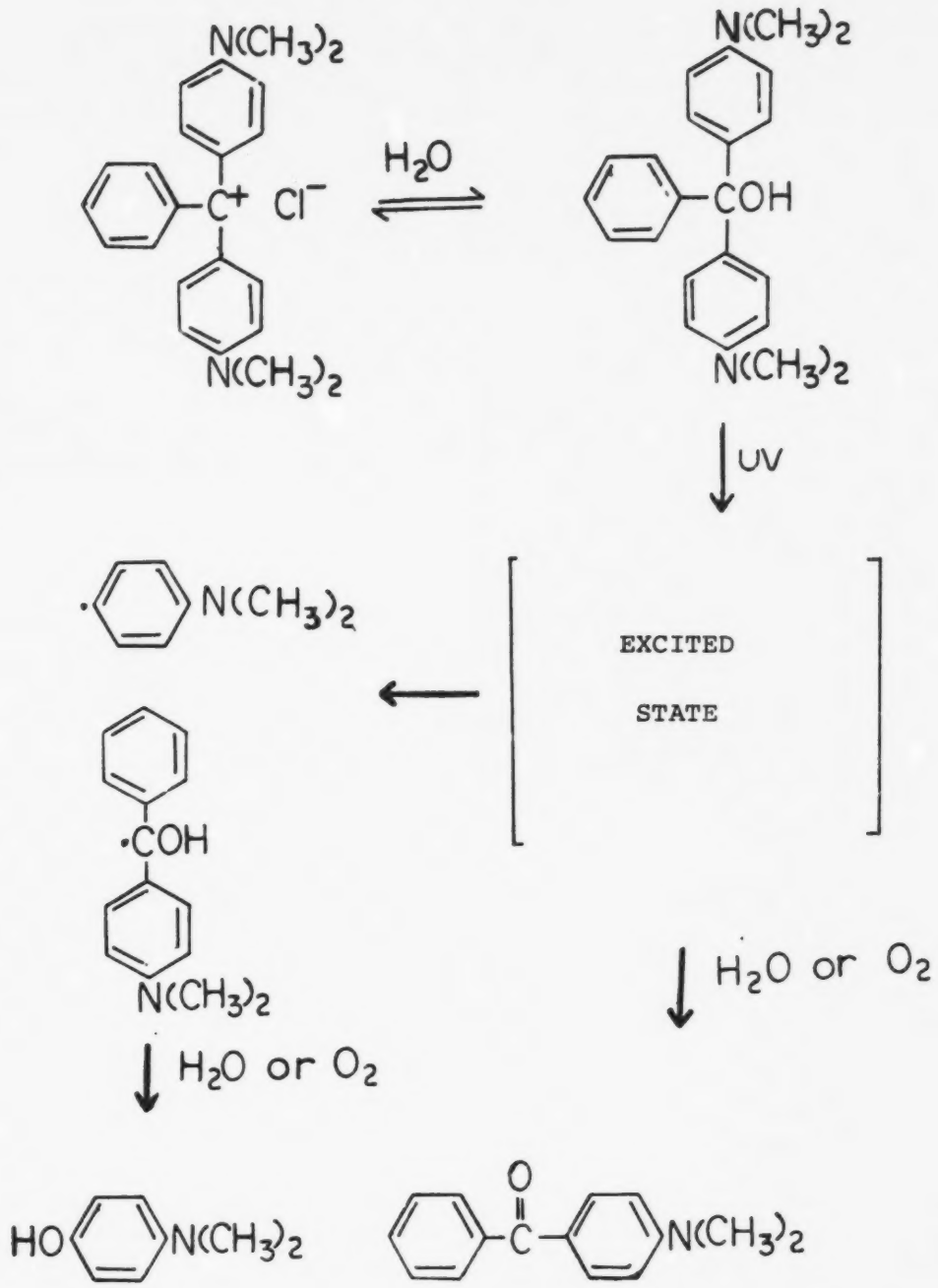


Figure 11 Mechanism for Degradation of Basic Green 4

Basic Green 4 has two adsorption bands in the visible region. The band at 422 nm represents an energy of 67.8 kcal/mole, while the adsorption at 619 nm corresponds to an energy value of 46.2 kcal/mole. A third band exists in the near ultraviolet at 318 nm and is equivalent to 89.9 kcal/mole. The leuco carbinol form in Figure 10 which has been shown to be the fugitive species does not absorb visible light and therefore requires ultraviolet light for degradation. Visible light can degrade dyes--McLaren[10] found in a study of over one hundred dyes that the most fugitive examples were readily degraded by visible and ultraviolet light, with wavelengths longer than 600 nm being responsible for degradation in some instances.

The possibility of non-light-catalyzed hydrolysis was eliminated when an aqueous solution of CI Basic Green 4 was shown to undergo no significant change over an eight-day period at 65°C[11] in the absence of light.

The evidence for the triphenylmethane dyes shows that their rate of degradation is clearly pH dependent and inversely proportional to the hydronium ion concentration.[7] Since the dyes would commonly be found in natural water supplies or receiving streams at or near a neutral pH, the degradations were conducted at neutral pH.

One point worth noting is the stability of some of the degradation products to ultraviolet light as evidenced by their isolation. The toxic properties of these products should be determined since they would remain in the environment for much longer periods than the dye molecule.

Acid Dyes

Acid dyes have an ancient origin, dating back many centuries to the first use of natural dyes on wool fibers. The first recorded preparation of a synthetic acid dye was in 1771.[12] Woulfe synthesized picric acid from indigo with nitric acid. Because of their bright colors the dyes still have widespread use today.

Acid dyes are used for nylon, wool and acrylic fibers.[13] The nylon or wool fiber is dyed from a bath having a weight of 20 to 30 times that of the fabric. The fiber is placed into the warm dyebath and the dye is then added. The temperature is raised slowly to 200°F and if necessary acetic or sulfuric acid is added to exhaust the dye onto the fiber. If the dye tends to go onto the fiber too rapidly it may be necessary to add a retarding agent such as sodium sulfate. Several retarding or leveling agents are used with acid dyes.

These dyes are comparatively small molecules with one or more sulfonic acid groups attached to the organic substrate. They have good water solubility and may or may not be removed from a waste stream by a conventional biological waste treatment plant. Because of this and their high tinctorial color value it is important to be able to estimate their light stability in a natural water supply.

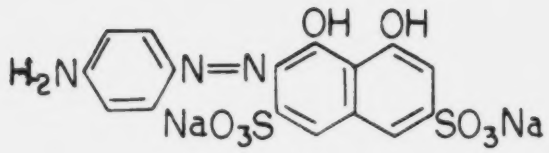
The acid dyes as a class have poor light fastness on textile fibers compared to vat or disperse dyes. This suggests that their photodegradation in water would be quite significant. Structures of acid dyes used in this study are shown in Figures 12 and 13. The curves for their fading rates are shown in Figures 14 to 20. Of the seven dyes studied, three showed drastic photo-induced degradation.

One generalization indicated here is that the acid azo dyes are more fugitive to light than the acid anthraquinone dyes (Violet 43 and Blue 40). An exception is the Acid Black 52 which is really a premetalized azo acid dye and is not comparable because of the known stability metal coordination adds to any dyestuff.[14]

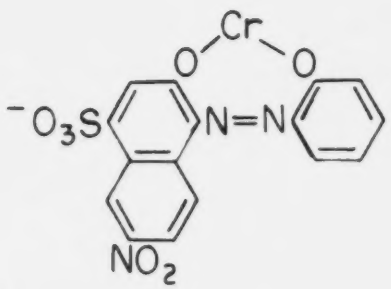
A detailed interpretation of the data is difficult. Acid Red 1, Figure 14, was stable and Acid Violet 3, Figure 15, and Acid Red 37, Figure 17, were completely degraded. This may be explained by the susceptibility of the primary amine group to oxidative attack. Why Acid Orange 10, Figure 16, was also degraded cannot be explained on this basis because it has no vulnerable amine group. The primary amine appears to be less labile when it is attached to the anthraquinone structure as is illustrated by the curve for Acid Blue 40 shown in Figure 20.

The basic reason for the degradation of the acid dyes seems to be their susceptibility to electrophilic attack. This has been demonstrated with the basic dyes and shown to be applicable to the reactions of oxidizing reagents with other dyes.[15] The more electron attracting groups that are present on the dye molecule generally the more stable it is to light.[16]

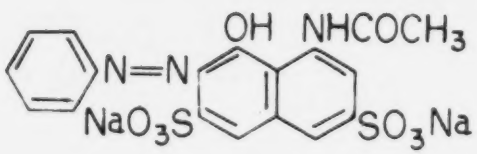
Acid dyes should be one of the best classes for which to interpret a fading mechanism because they are water soluble and give homogenous solutions. This is not true for the disperse, vat and sulfur dye classes which can undergo physical changes which affect the



Acid Violet 3 C.I. 16580

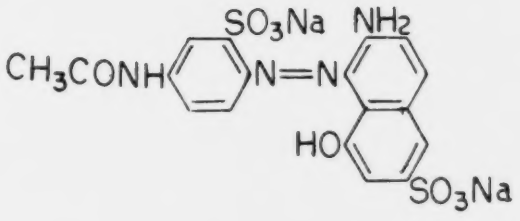


Acid Black 52 C.I. 15711

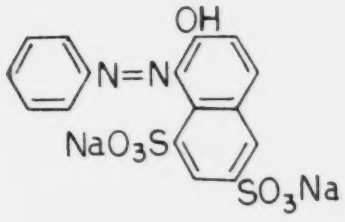


Acid Red 1 C.I. 18050

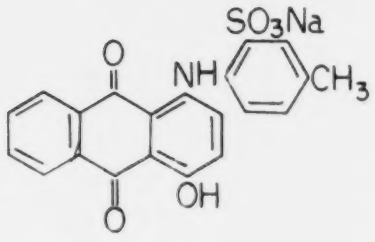
Figure 12 Structures of Acid Dyes Studied



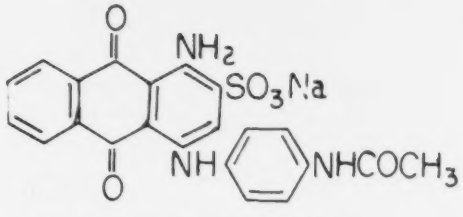
Acid Red 37 C.I. 17045



Acid Orange 10 C.I. 16230



Acid Violet 43 C.I. 60730



Acid Blue 40 C.I. 62125

Figure 13 Structures of Acid Dyes Studied

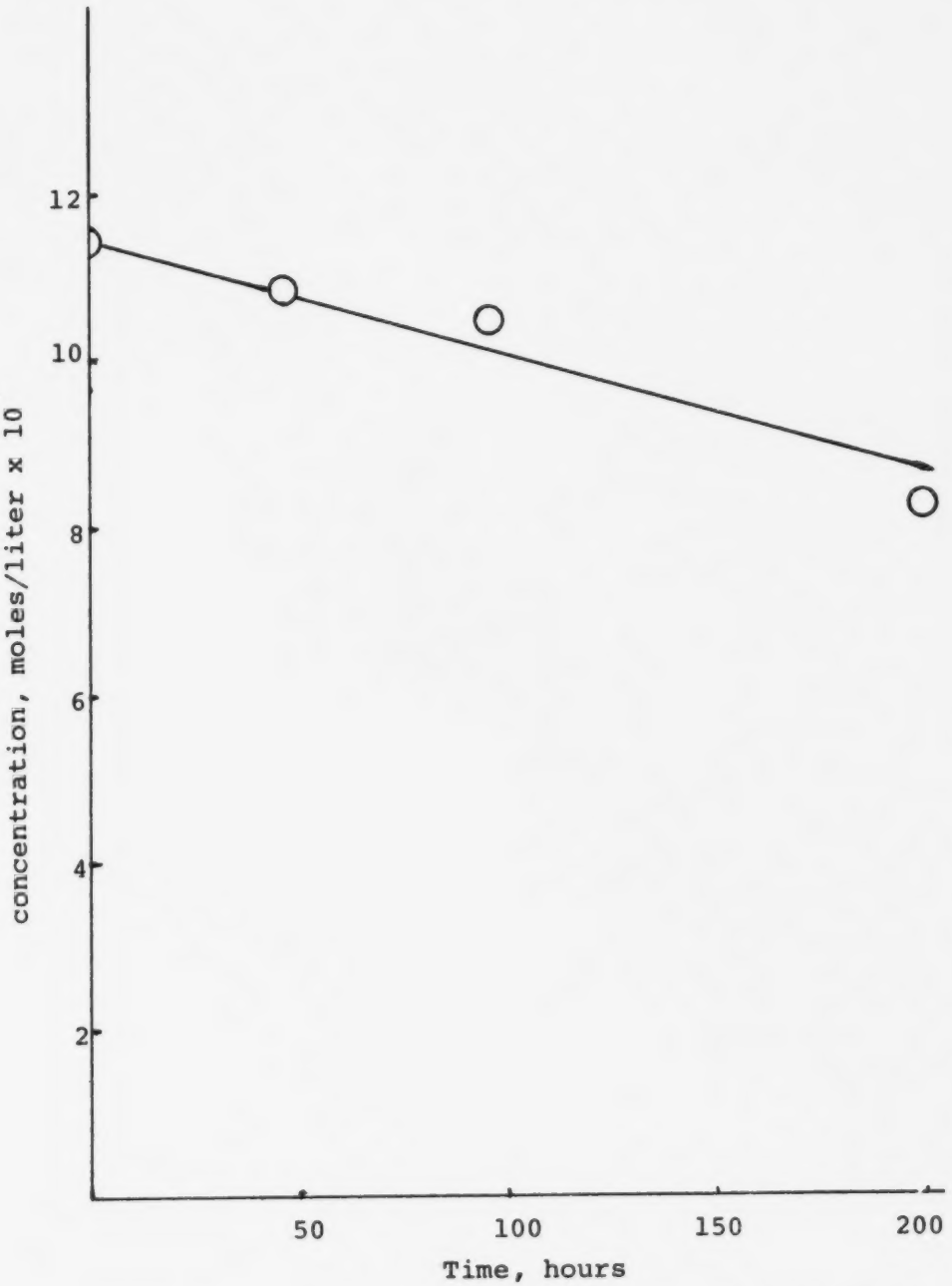


Figure 14 Rate of Photodegradation of Acid Red 1 in water at 50 °C.

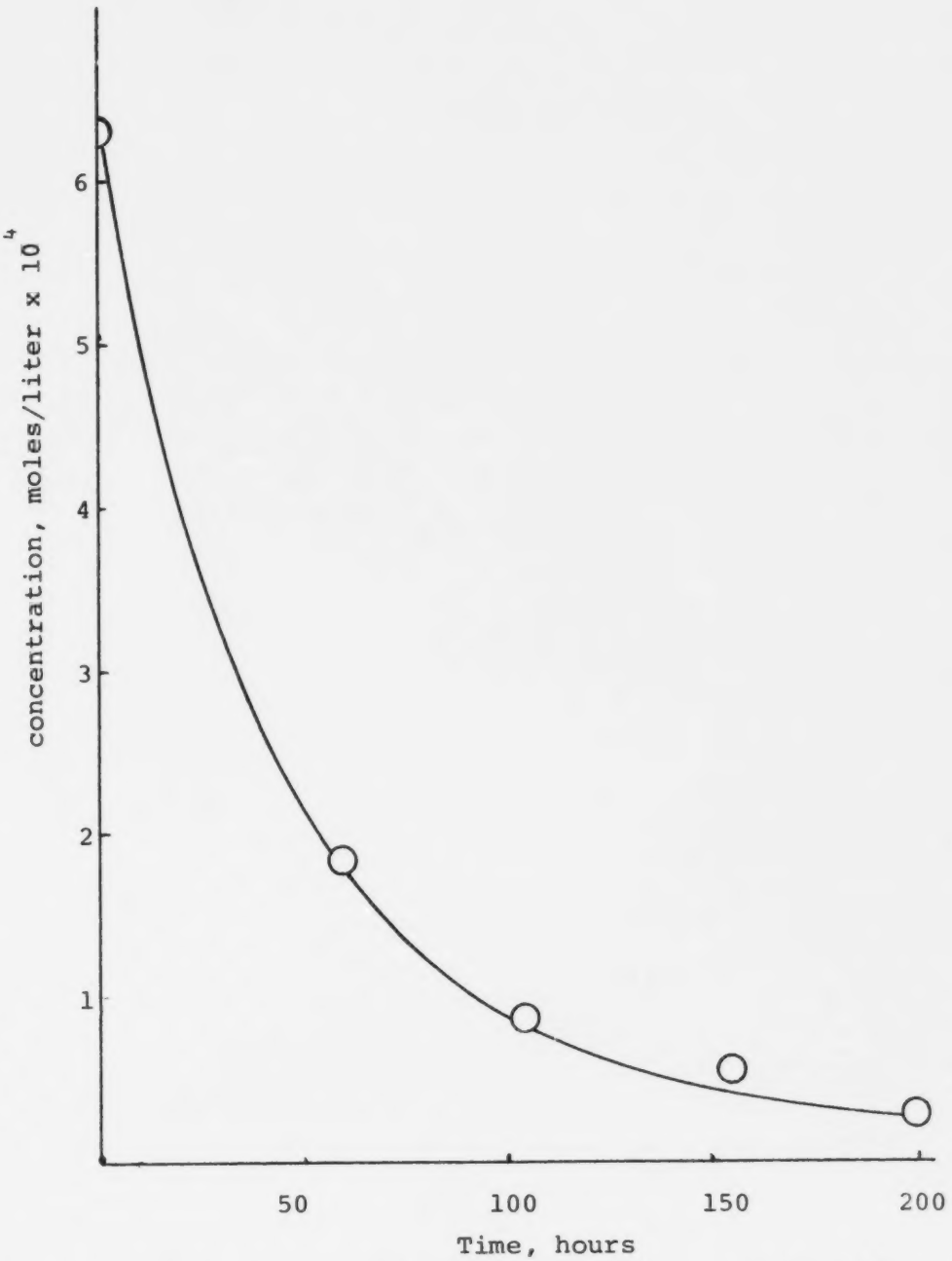


Figure 15 Rate of Photodegradation of Acid Violet 3 in water at 50°C.

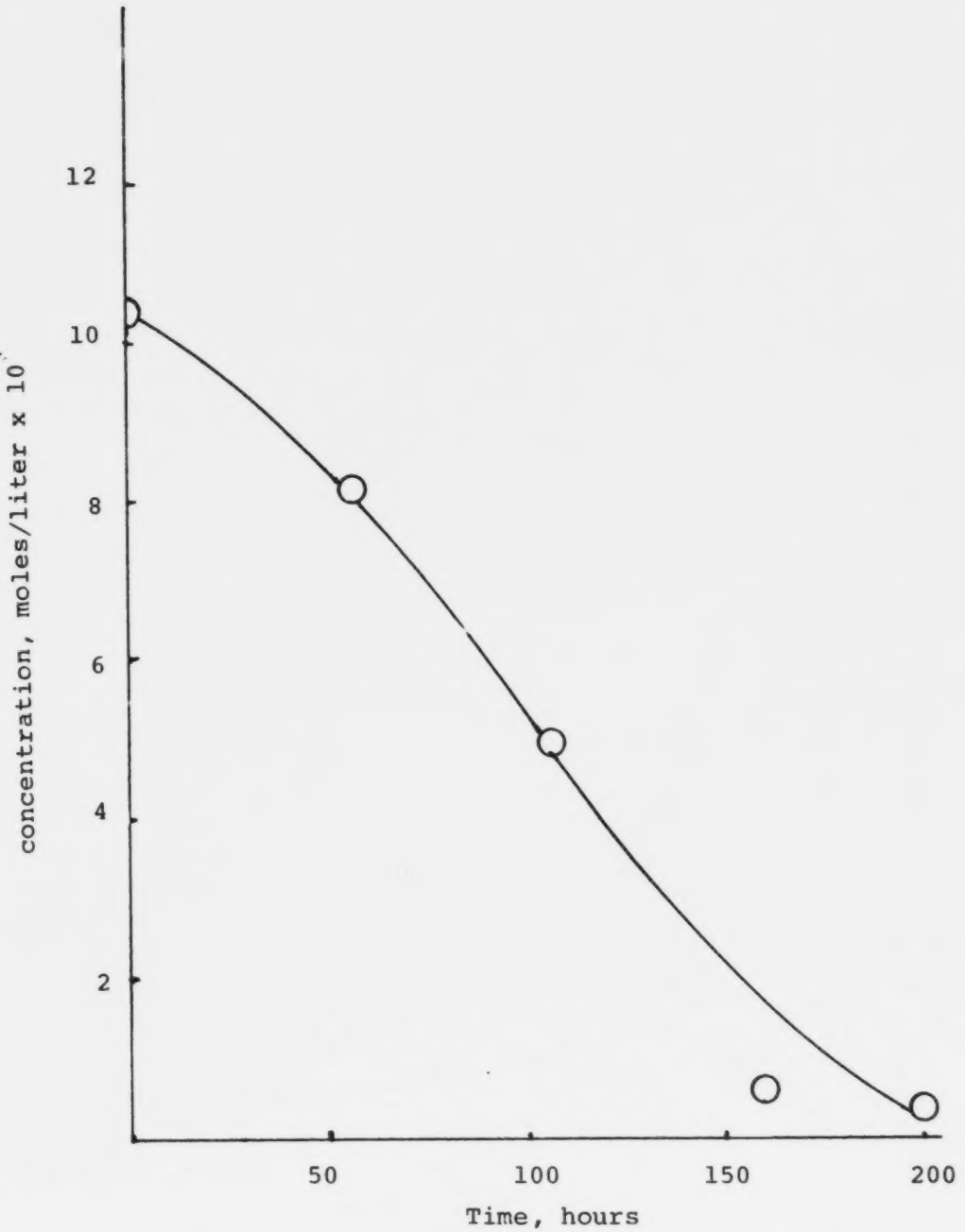


Figure 16 Rate of Photodegradation of Acid Orange 10 in Water at 50°C.

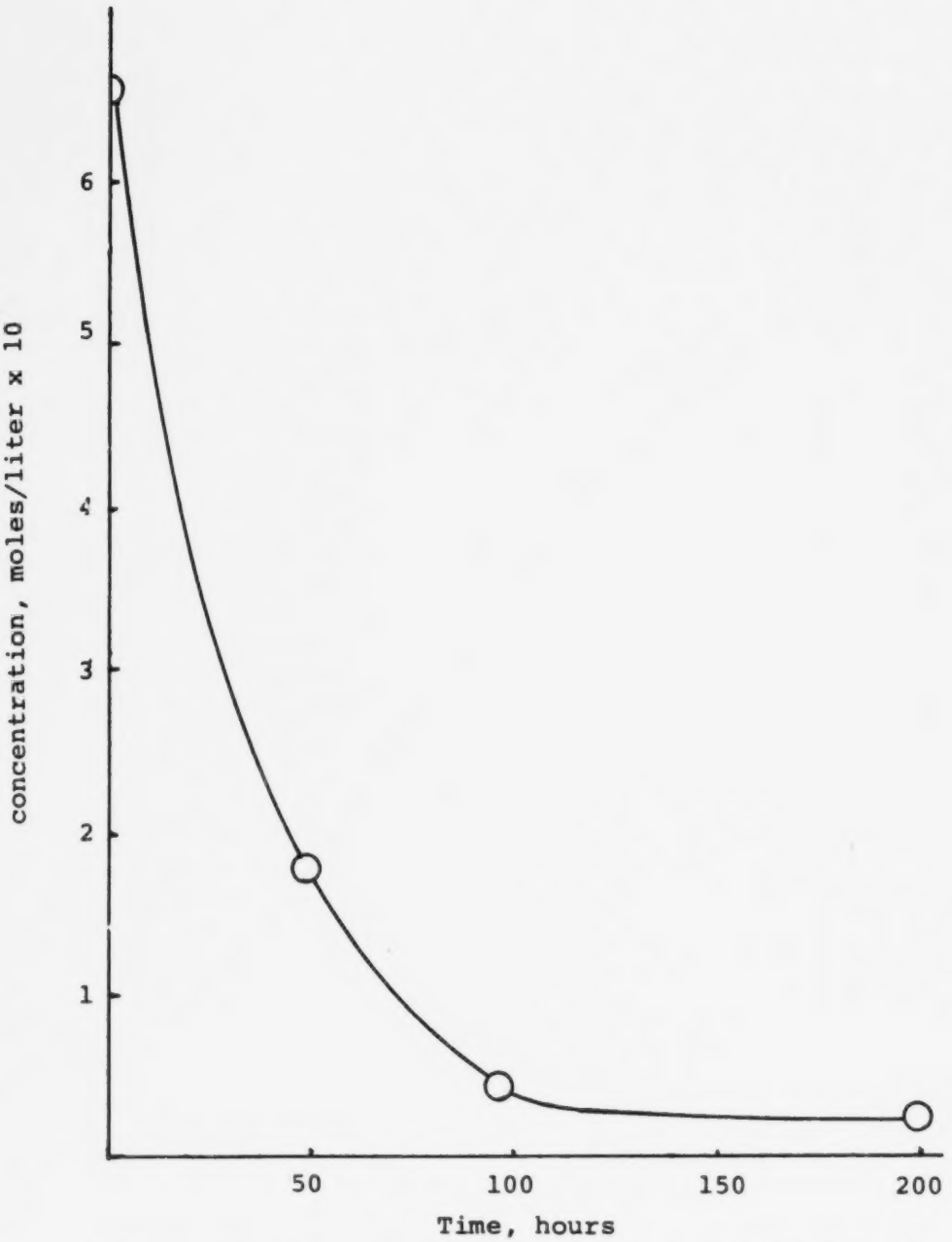


Figure 17 Rate of Photodegradation of Acid Red 37 in Water at 50°C.

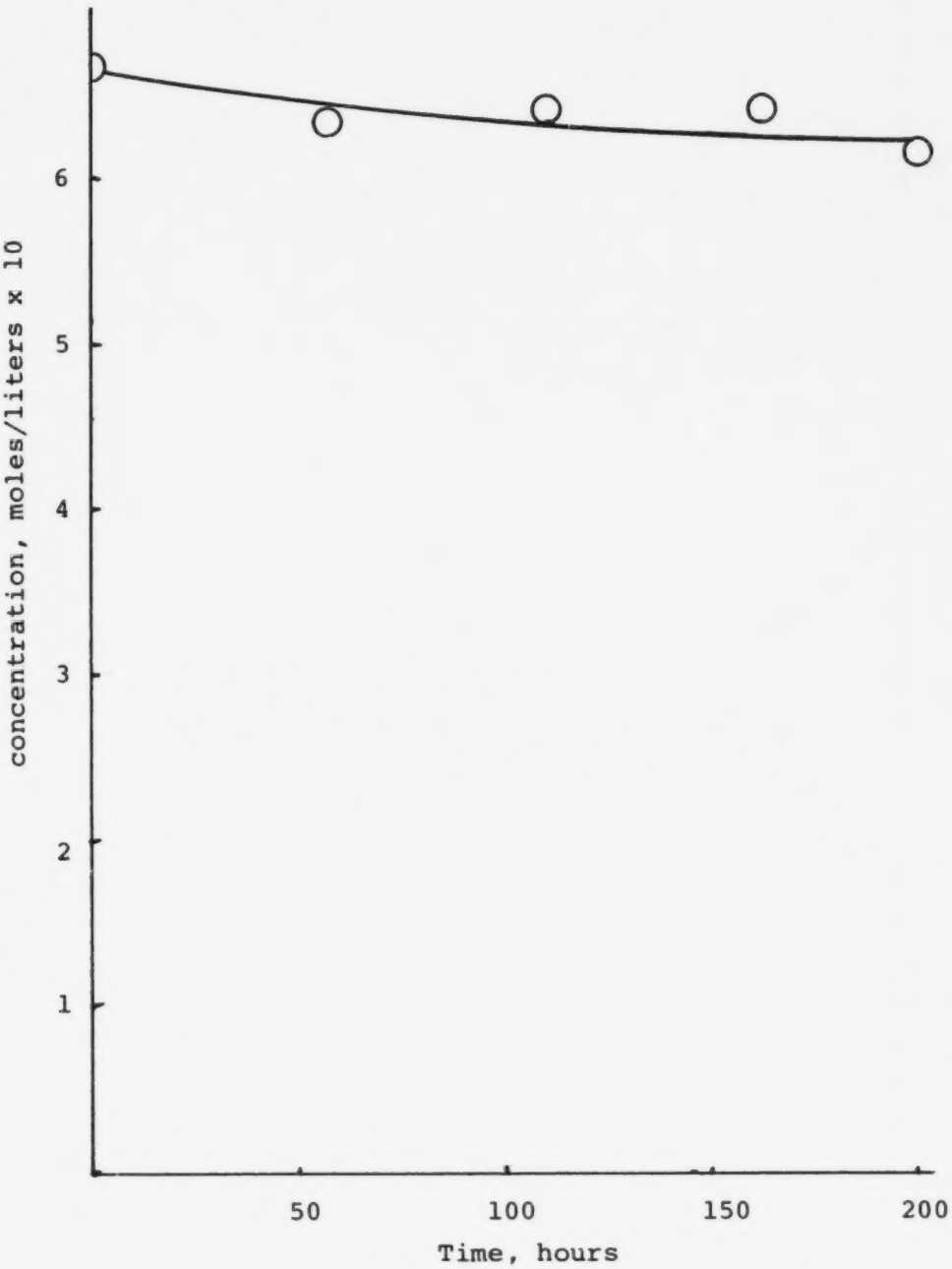


Figure 18 Rate of Photodegradation of Acid Black 52 in Water at 50°C.

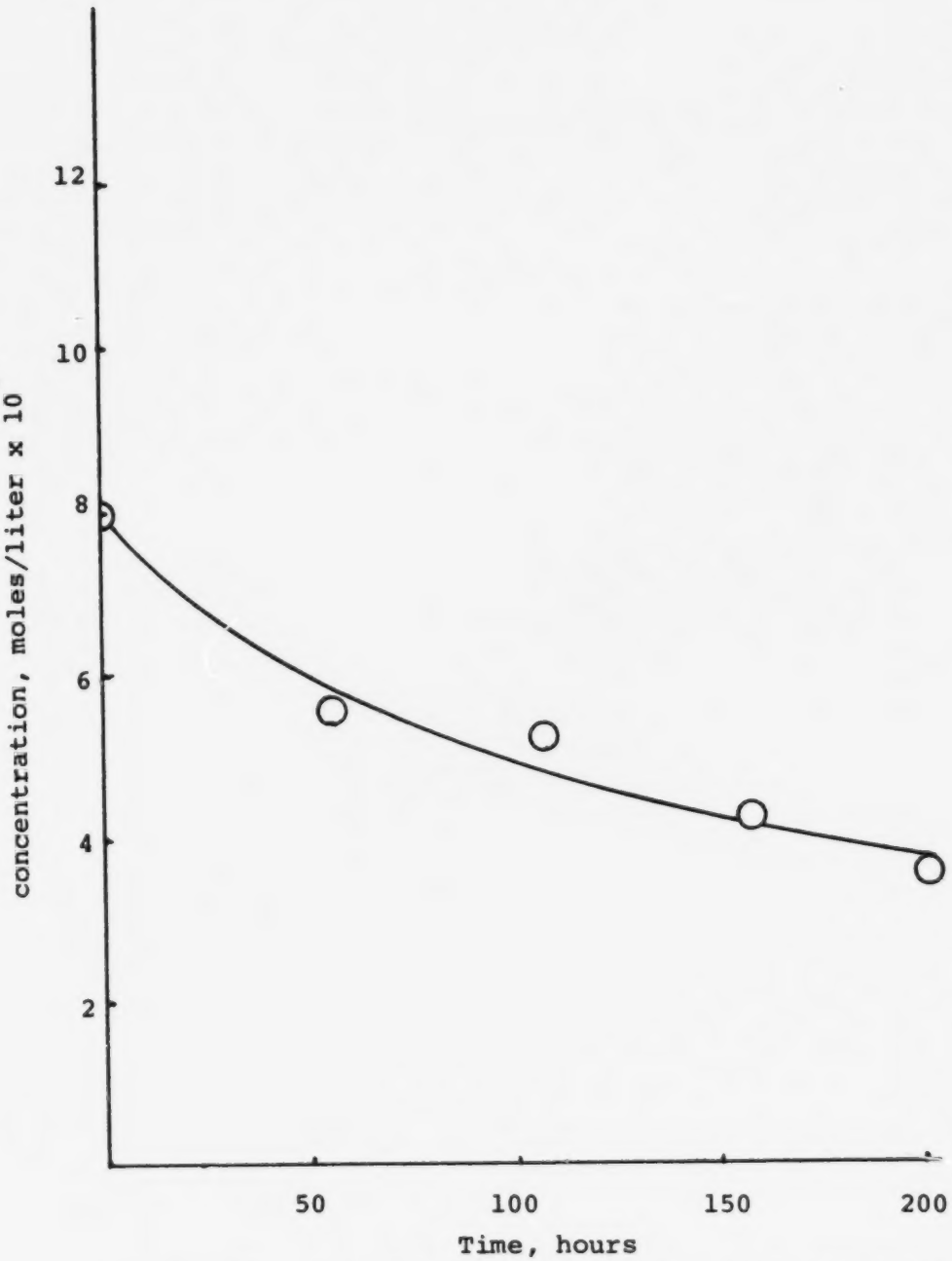


Figure 19 Rate of Photodegradation of Acid Violet 43 in Water at 50°C.

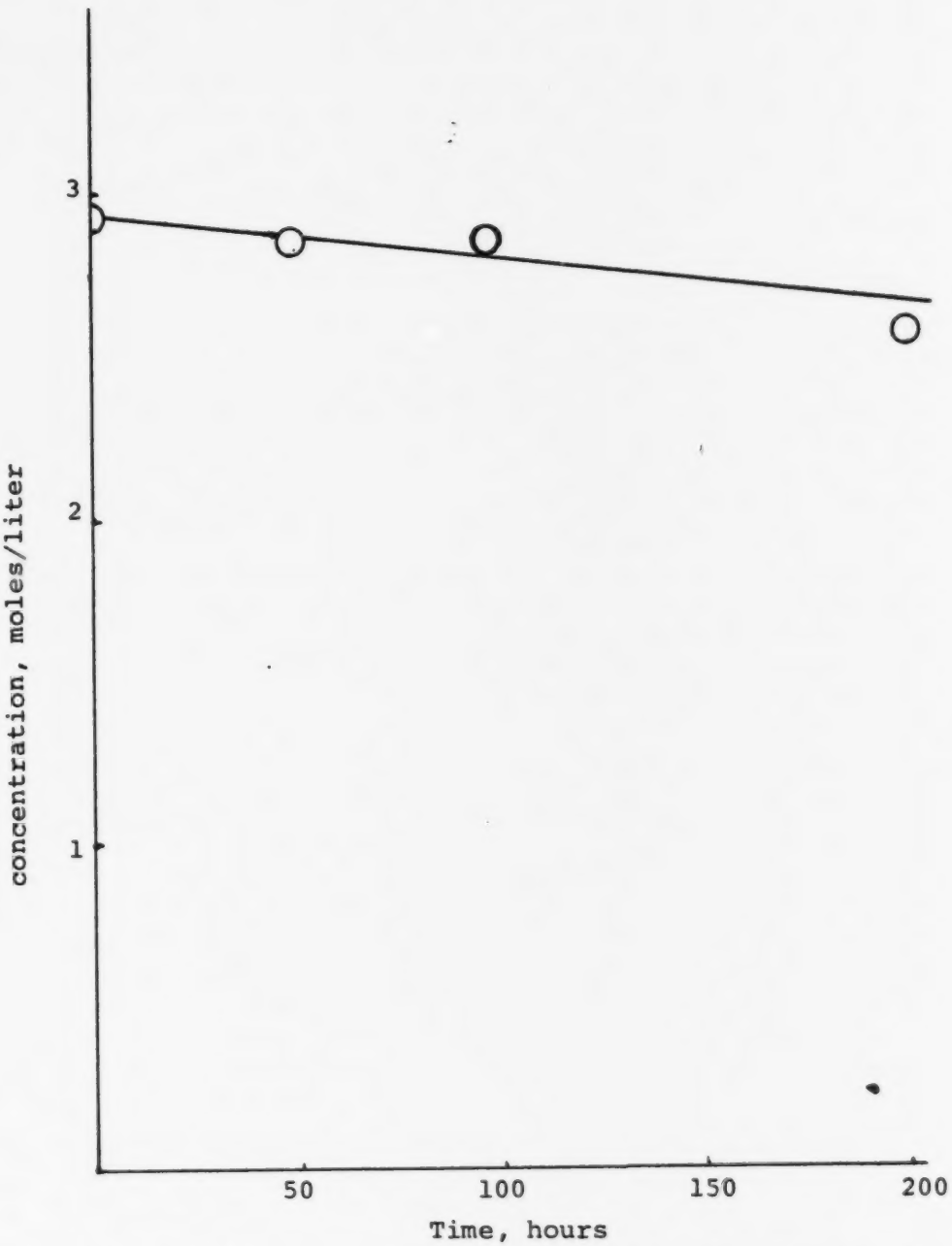


Figure 20 Rate of Photodegradation of Acid Blue 40 in Water at 50°C.

absorption of light without undergoing any chemical degradation. These dyes are discussed later.

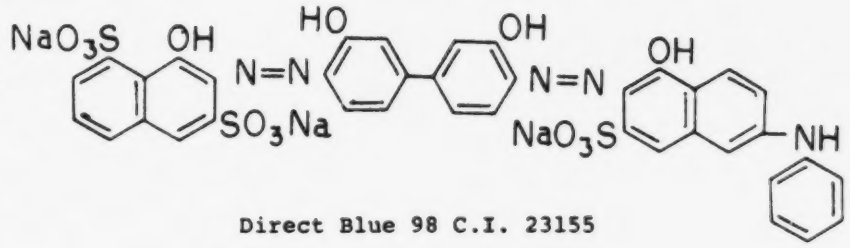
Attempts to isolate degradation products from the acid dyes were unsuccessful. Degradation products such as phenol or aniline were either volatilized from the reaction cell during the study or were degraded themselves since no low molecular weight products were detected by gas chromatographic or mass spectral analyses of the final concentrated solutions. Evidently the ionic degradation products were not volatile enough for analysis by GC or MS, and preparation of their diazomethane derivatives was unsuccessful. Additional work in this area might lead to characterization of some of the degradation products.

Direct Dyes

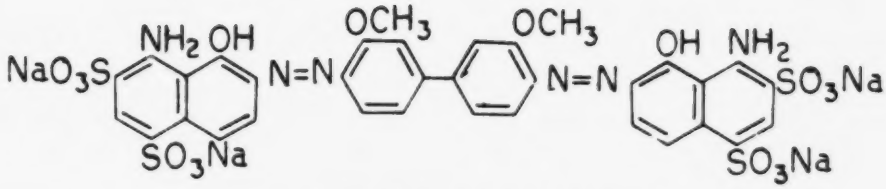
The direct dyes are one of the major classes of dyes used on cellulose fibers. The dyes are applied from a water bath about 30 times the weight of the fabric being dyed. After the fabric and dyes are placed in the bath, it is heated to near boiling and a salt is added to exhaust the dye onto the fiber. The amount of salt required varies from dye to dye but is approximately 10 percent of the weight of fabric being dyed.

The dyes were chosen on the basis of use by the textile industry--their structures are shown in Figures 21 and 22. They are more resistant to light degradation than the basic or acid dyes previously discussed as can be seen by the fading rate curves shown in Figures 23 to 30.

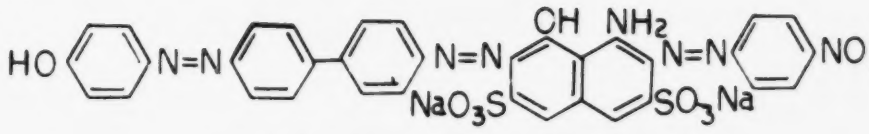
Only two of the direct dyes, Direct Blue 76 and Direct Red 83, lost greater than 50 percent of their optical density after 200 hours exposure to artificial light. This is not unusual as the direct dyes have better light fastness properties on textile fibers than the acid or basic colors. After exposure, no volatile degradation products could be detected in the concentrated dye solutions by gas chromatographic or mass spectral analyses. Attempts to prepare methyl ester derivatives of the expected ionic degradation products by treatment with diazomethane yielded nothing detectable by mass spectral or gas chromatographic analyses. As was the case with the acid dyes, the low molecular weight products were destroyed or volatilized during exposure and the high molecular weight products had too low a vapor pressure to allow separation and identification.



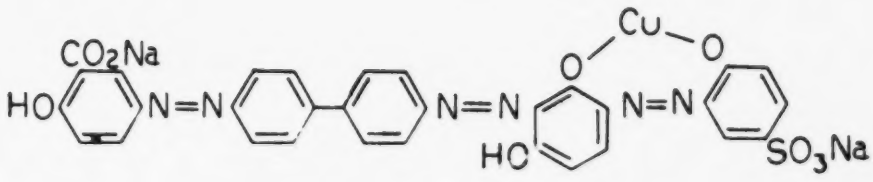
Direct Blue 98 C.I. 23155



Direct Blue 76 C.I. 24410

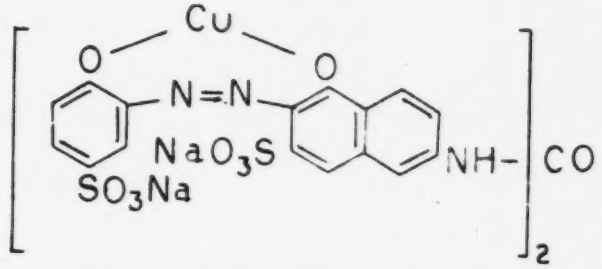


Direct Green 6 C.I. 30295

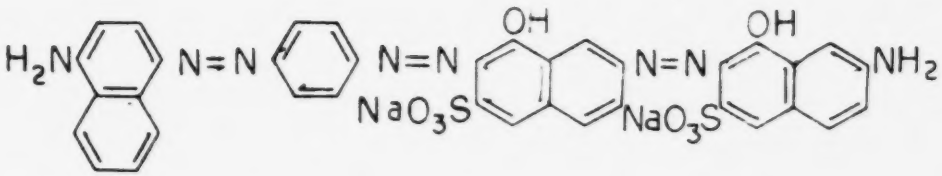


Direct Brown 95 C.I. 30145

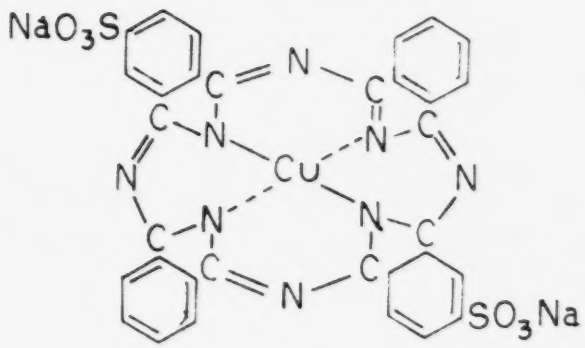
Figure 21 Structures of Direct Dyes Studied



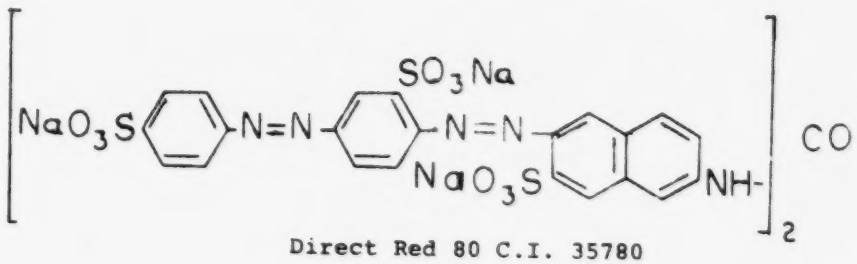
Direct Red 83 C.I. 29225



Direct Black 80 C.I. 31600



Direct Blue 86 C.I. 74180



Direct Red 80 C.I. 35780

Figure 22 Structures of Direct Dyes Studied

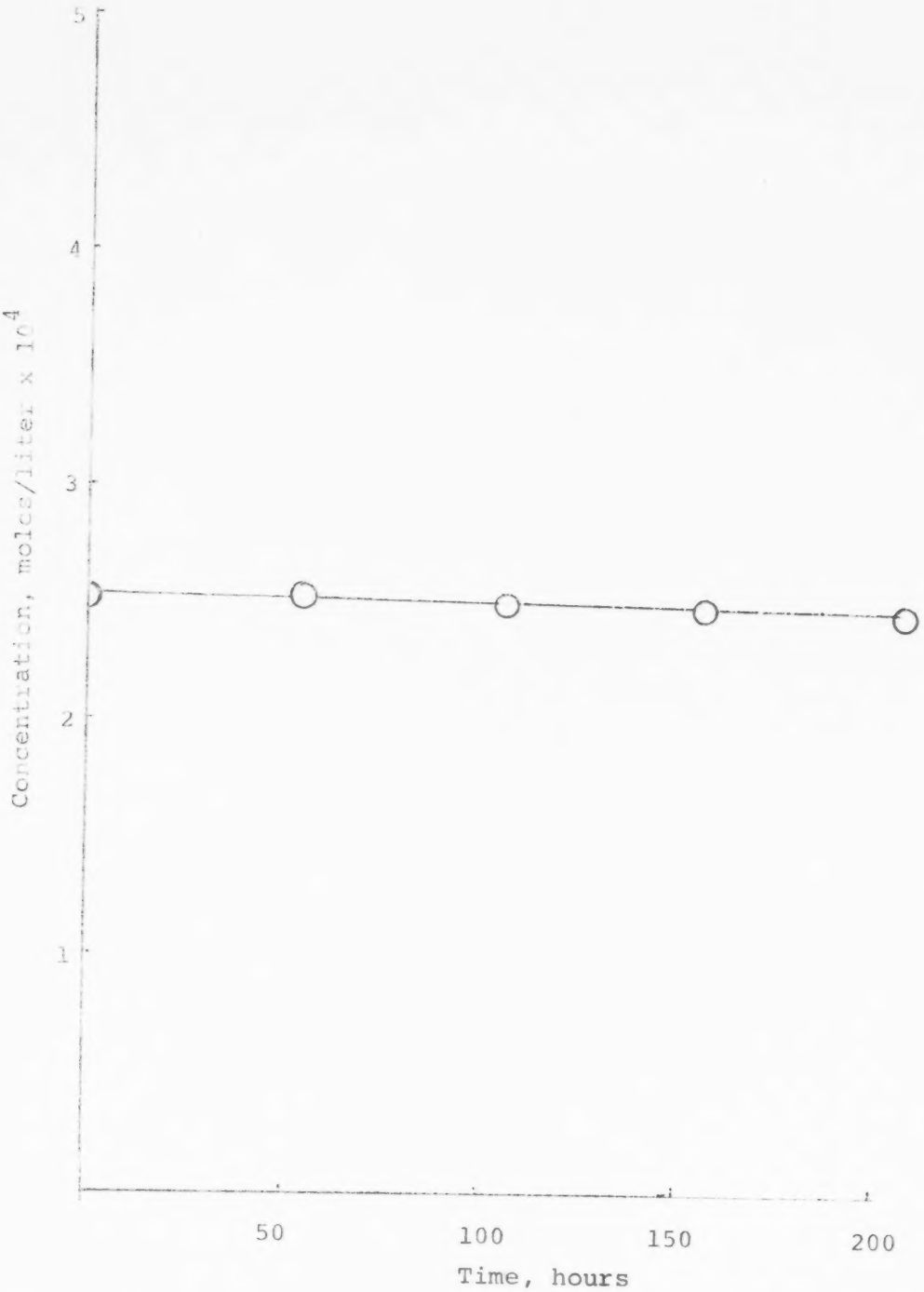


Figure 23 Rate of Photodegradation of Direct Red 80 in Water at 50°C.

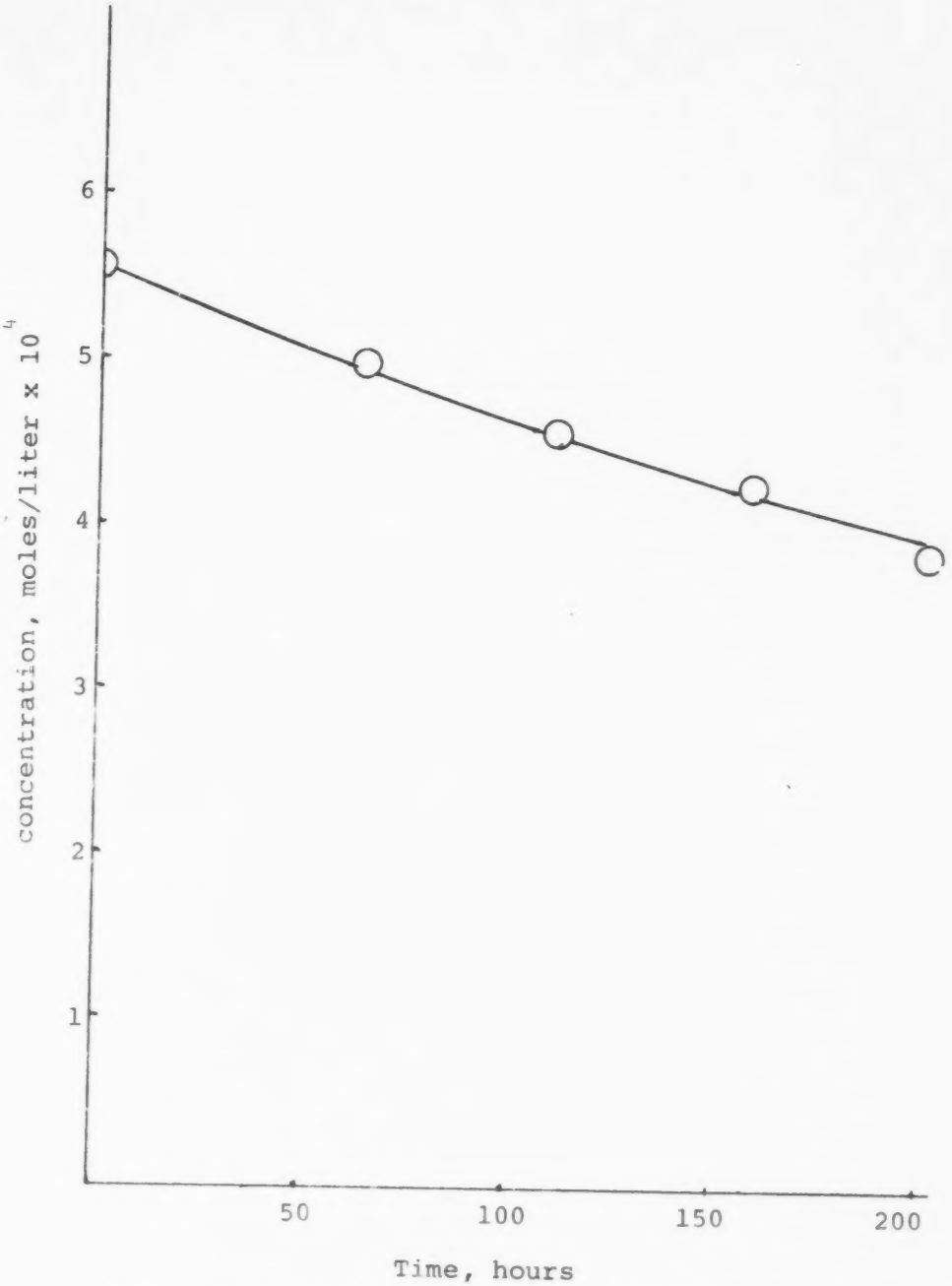


Figure 24 Rate of Photodegradation of Direct Green 6 in Water at 50°C.

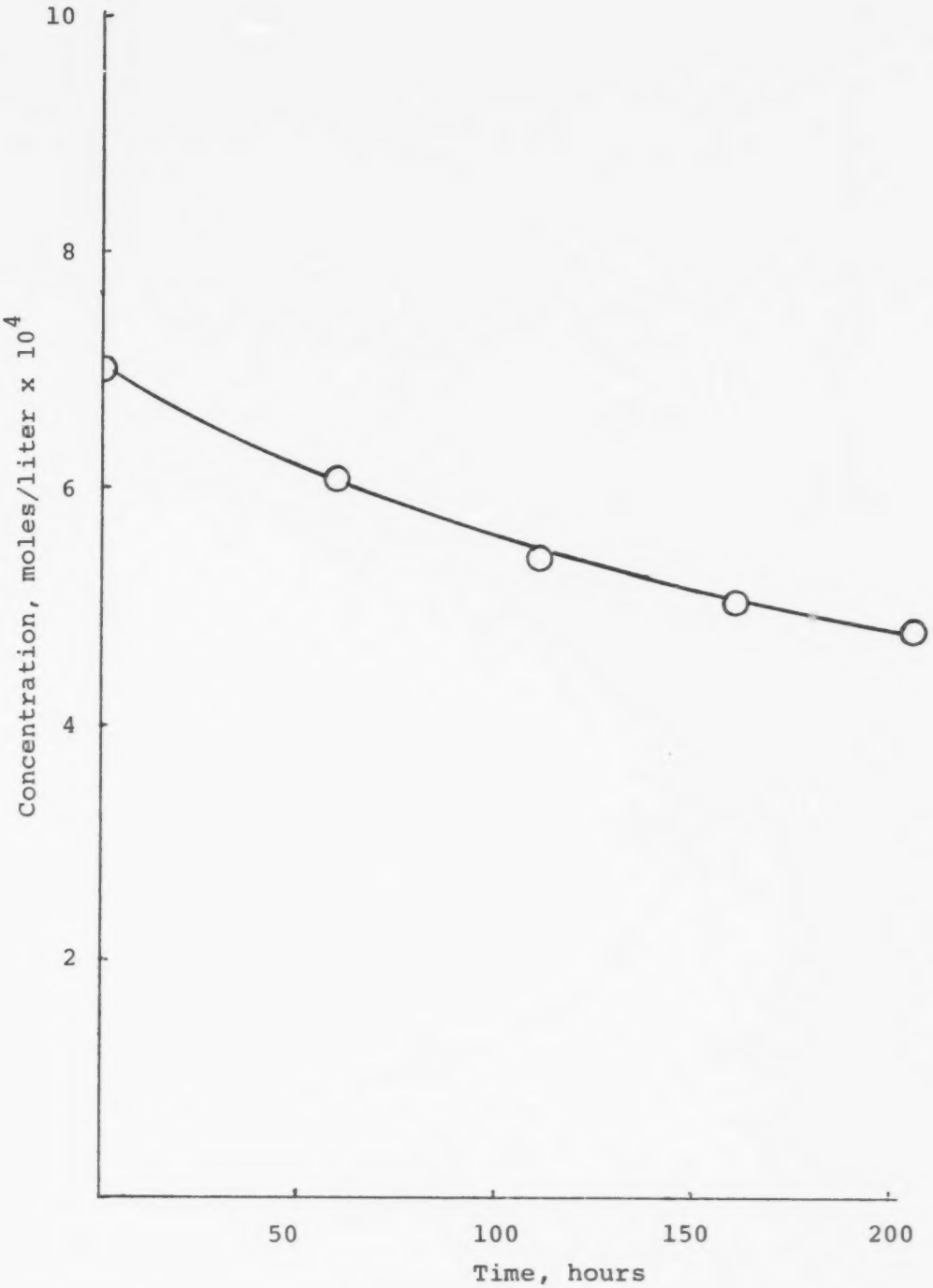


Figure 25 Rate of Photodegradation of Direct Black 80 in Water at 50°C.

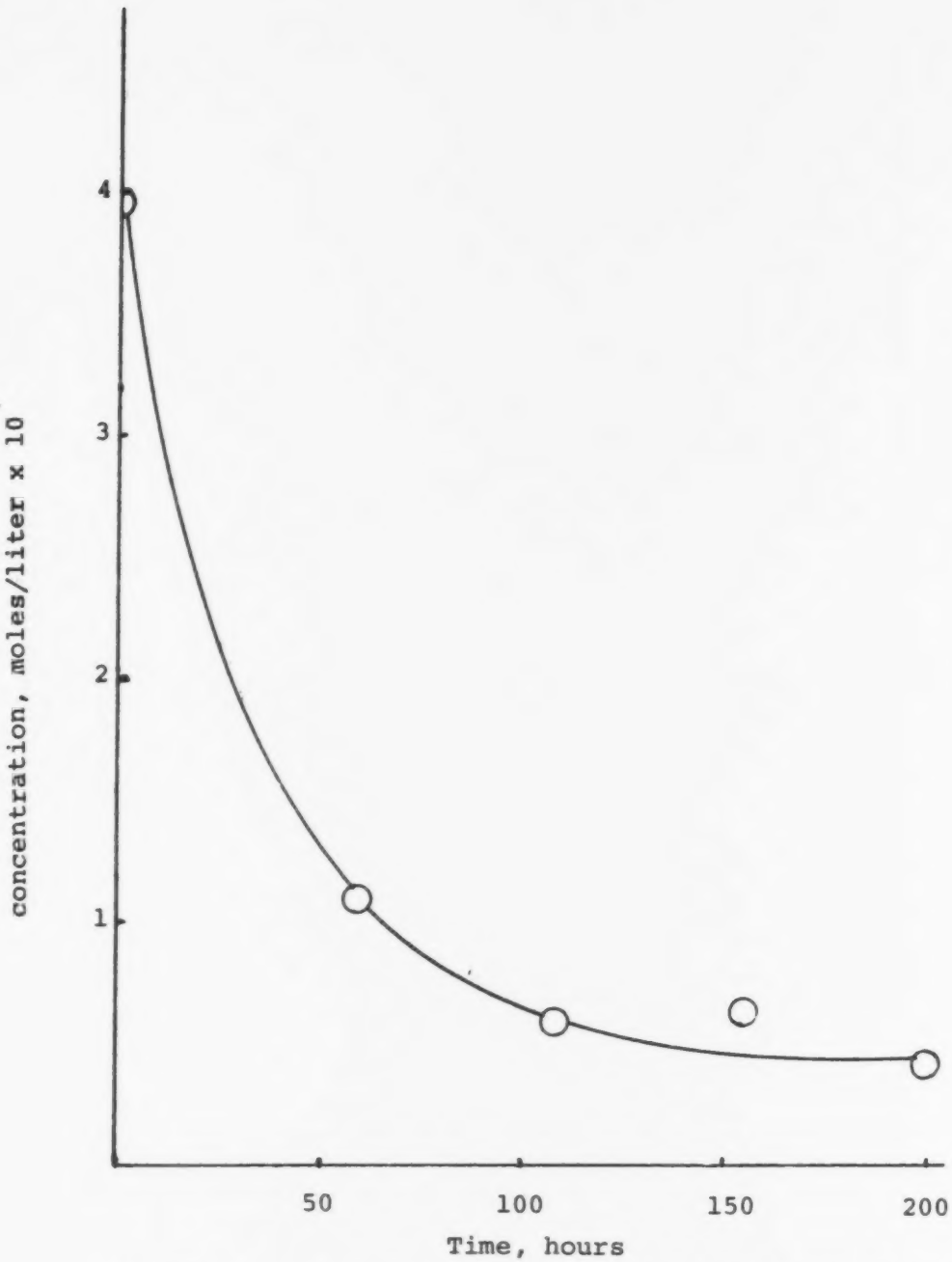


Figure 26 Rate of Photodegradation of Direct Blue 76 in Water at 50°C.

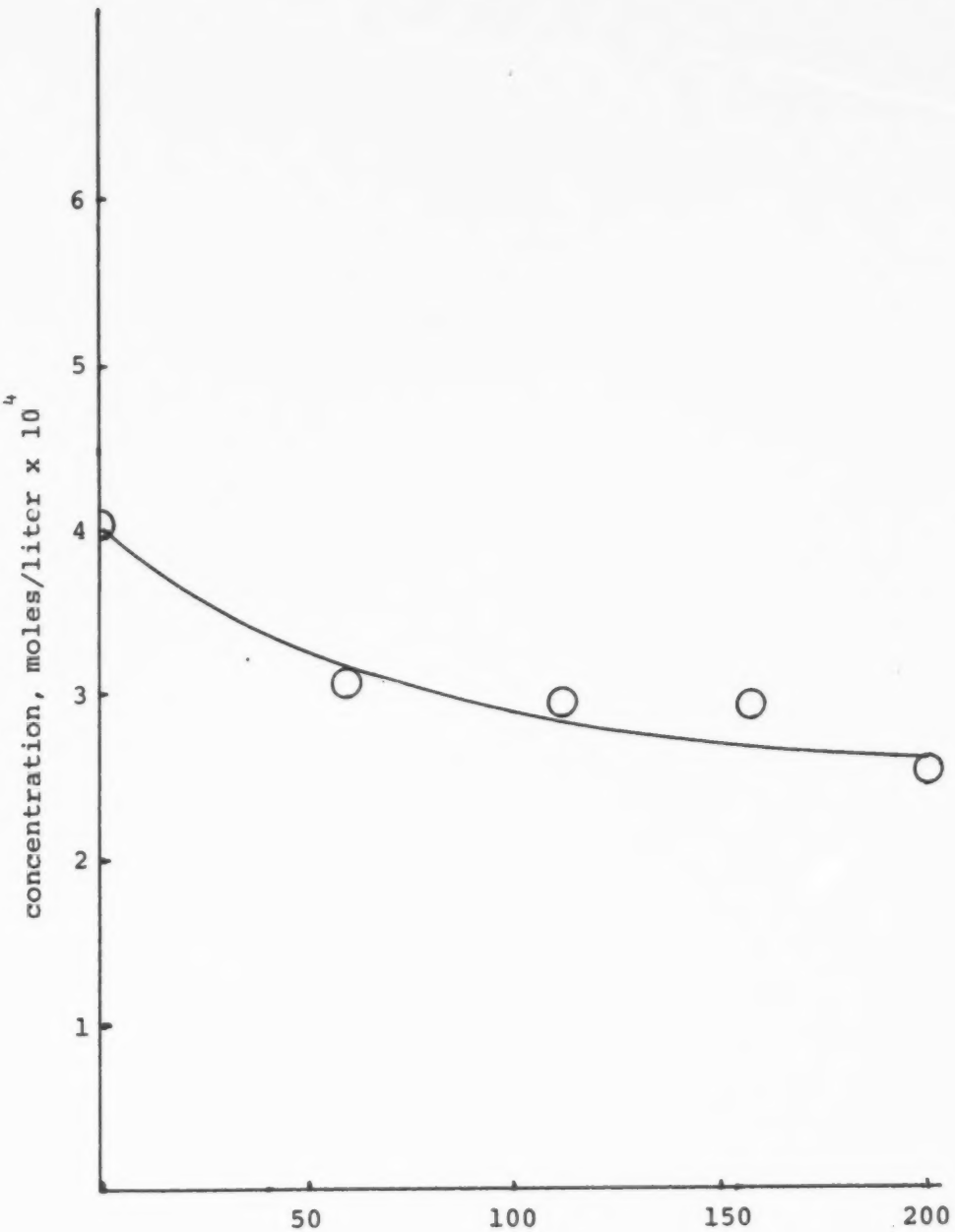


Figure 27 Rate of Photodegradation of Direct Blue 98 in Water at 50°C.

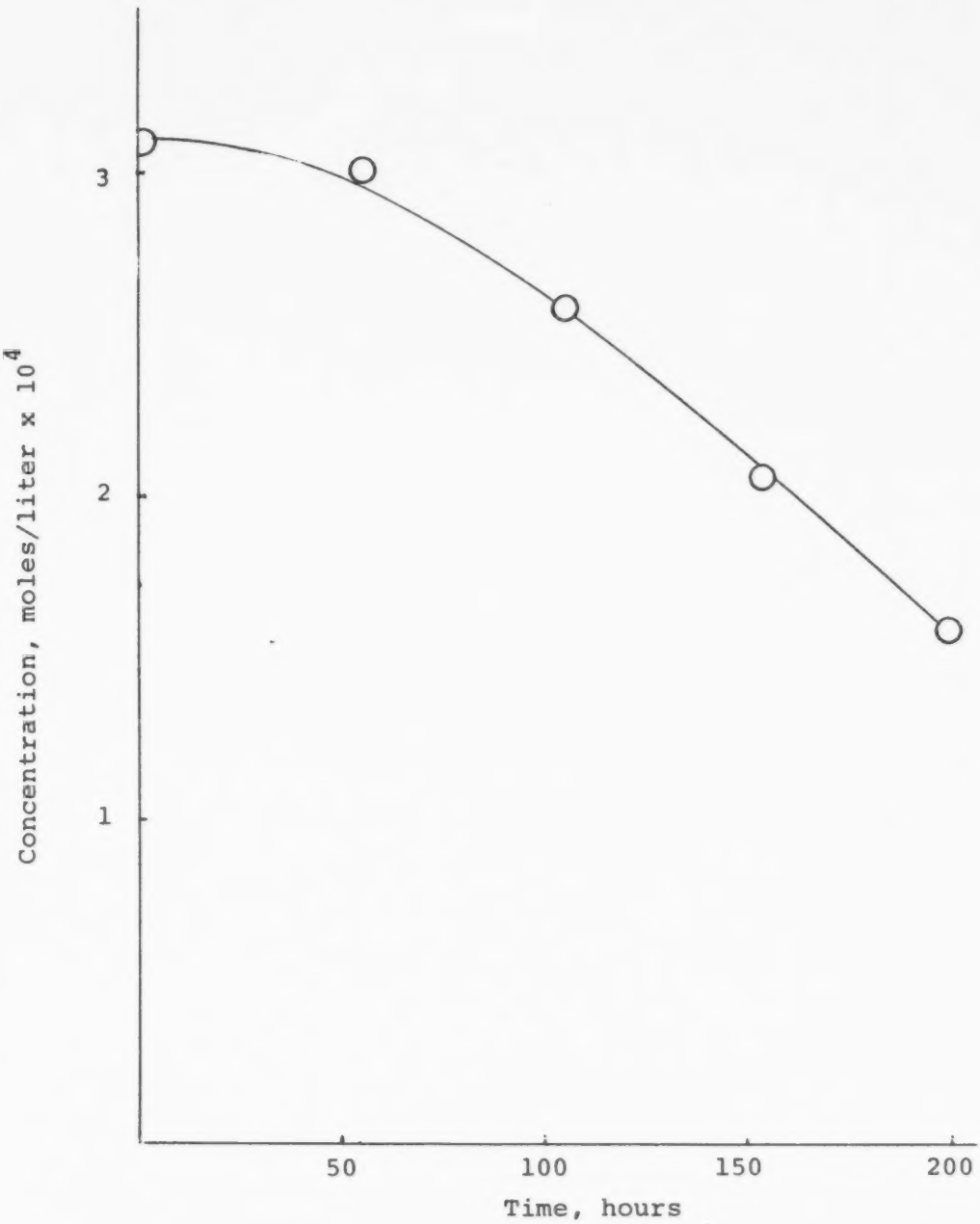


Figure 28 Rate of Photodegradation of Direct Red 83 in Water at 50°C.

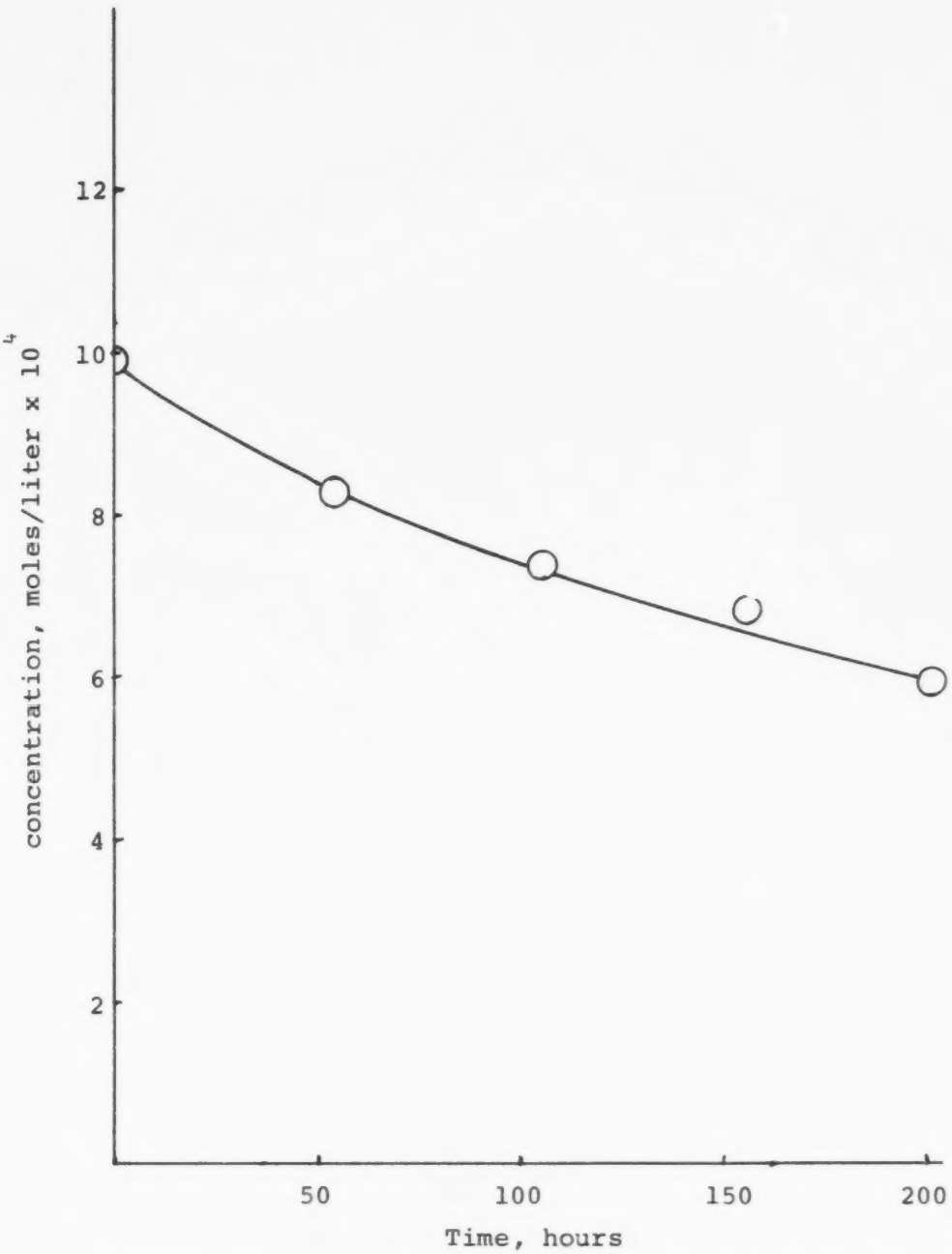


Figure 29 Rate of Photodegradation of Direct Brown 95 in Water at 50 °C.

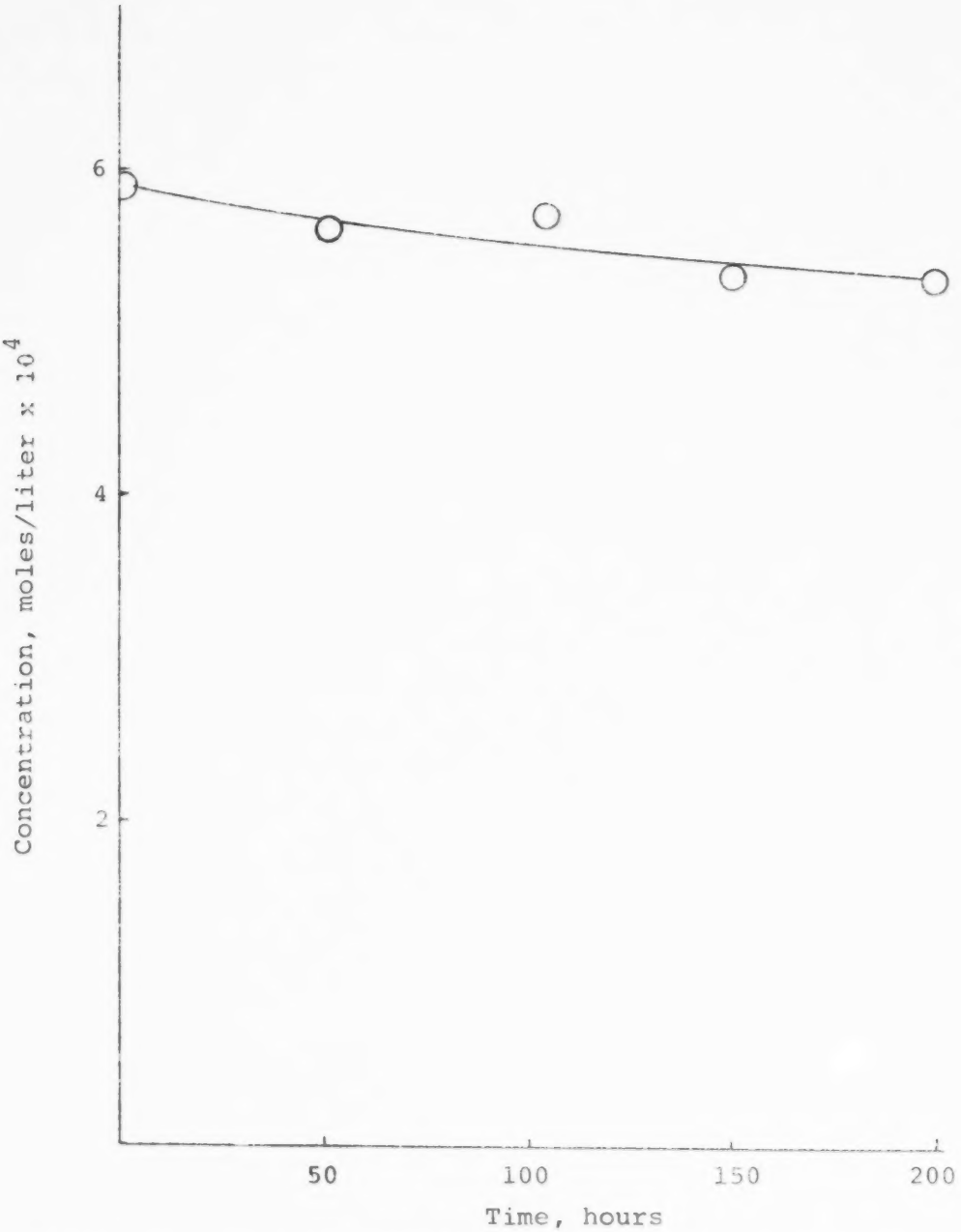


Figure 30 Rate of Photodegradation of Direct Blue 86 in Water at 50°C.

Some of the direct dyes would have sufficient affinity for the sludge in a biological waste treatment plant to be adsorbed and removed from the wastewater. Others would require chemical or physical treatment for their removal. In any case the data show that most direct dyes would be stable and resist photochemical degradation in a treatment plant or receiving water.

The comparison between degradation by natural and artificial light can be seen in Figure 31. The data show that the rate of degradation is at least 10 times as slow in natural daylight as in artificial light. This indicates that the direct dyes are very stable in natural waters.

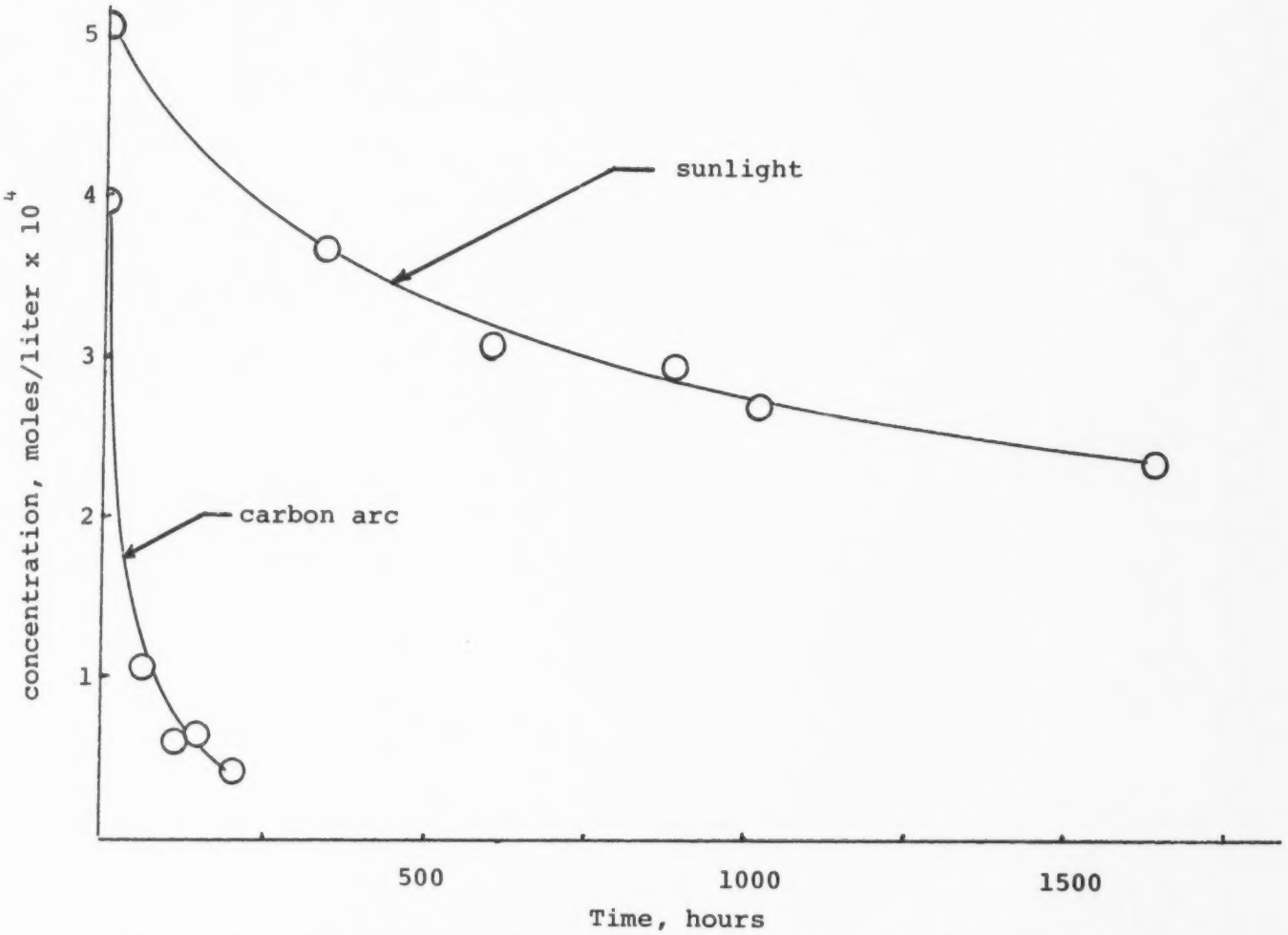


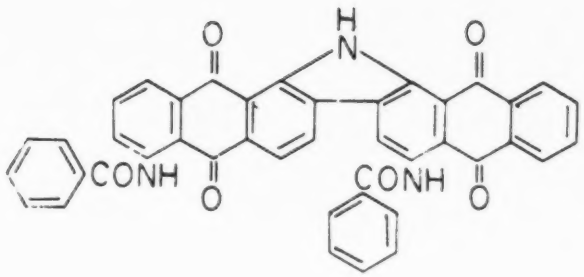
Figure 31 Rate of Photodegradation of Direct Blue 76 in Water Exposed to Sunlight and Carbon Arc light

Vat Dyes

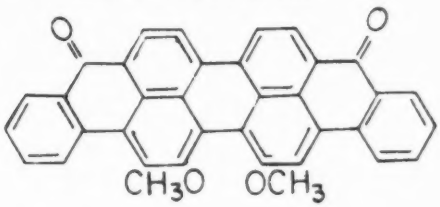
Vat dyes are applied to cellulose fibers by batch and continuous processes. The vat dye is a nonionic water insoluble pigment that must be reduced to a soluble anionic leuco form with sodium hydrosulfite. The bath from which the dye is applied varies in volume, is alkaline and contains dispersing agents, sodium sulfite and excess sodium hydrosulfite. After the dye is adsorbed on the fiber it is oxidized to the insoluble form with a common oxidizing agent. If the dyes are applied by continuous processes the chemicals which are used are the same but require much less water.

The structures of the vat dyes used for this study are shown in Figure 32. Vat dyes are applied almost exclusively on cellulose fibers. They are noted for their resistance to light degradation,[17] and were found to be fairly stable in this study as the curves in Figures 33 to 36 show. The dyes did show up to 40 percent color loss after 200 hours exposure to artificial light. This was not completely due to decomposition of the dye, but partly to aggregation of the dispersion.[18] This is supported by the fact that the absorbency of all four dyes decreased to about the same extent in 200 hours--more difference would be expected if photochemical degradation was the only factor responsible. Vat dyes are sold as a pigment dispersion. The pigment particles are near one micron or less in size.[19] When the dispersion is warmed or heated over a period of time the small particles can coalesce into larger particles, causing the dispersion to have a lower optical density.[18] This may have occurred to some degree during exposure to the carbon arc and accounted for some of the tinctorial loss of the dye dispersions. Aliquots of the dispersion were taken and dissolved in dimethyl formamide for measurement. Complete solution of the dyes may not have occurred with dimethyl formamide and would become more difficult as the pigment particles grew larger during exposure, resulting in lower absorbency. This point is speculative, but pigment aggregation is a well established phenomenon with vat dyes.[18]

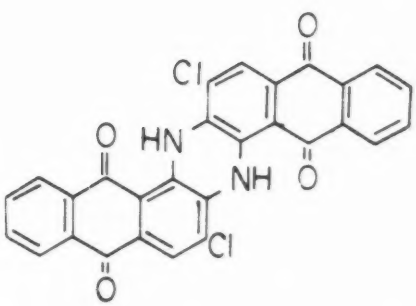
The residue remaining after degradation of Vat Blue 6, which is noted in the industry for its instability when compared to other vat dyes, was analyzed for chlorine to check for chemical changes upon ultraviolet exposure. The elemental analysis showed a 25 percent loss of chlorine which would account for at least 25 percent decomposition of the dye. The low volatility and solubility of the residues prevented successful mass spectral and chromatographic analyses of the degradation products.



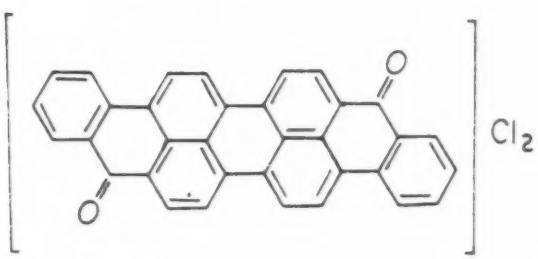
Vat Brown 3 C.I. 69015



Vat Green 1 C.I. 59825



Vat Blue 6 C.I. 69825



Vat Violet 1 C.I. 60010

Figure 32 Structures of Vat Dyes Studied

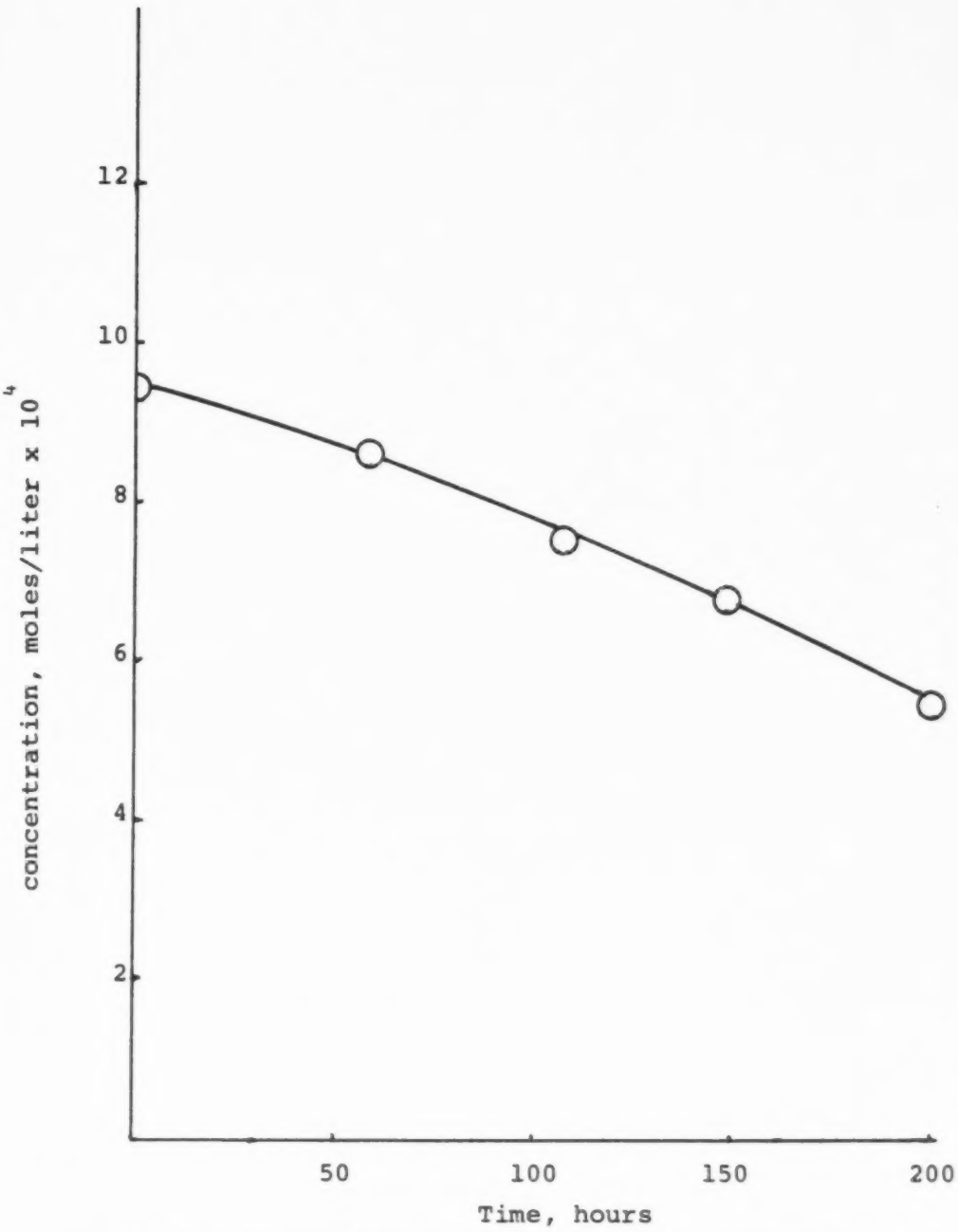


Figure 33 Rate of Photodegradation of Vat Brown 3 in Water at 50°C

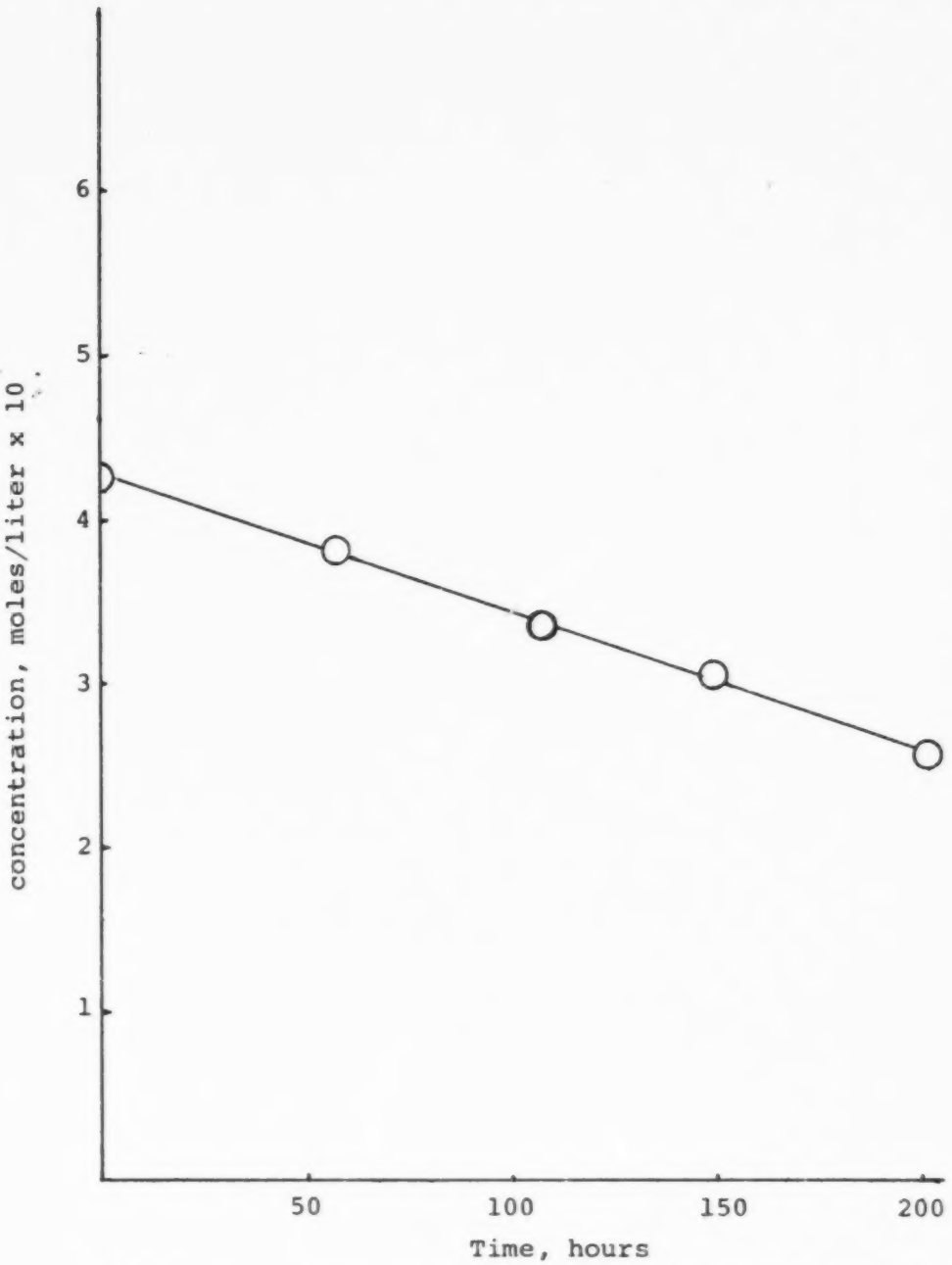


Figure 34 Rate of Photodegradation of Vat Violet 1 in Water at 50°C.

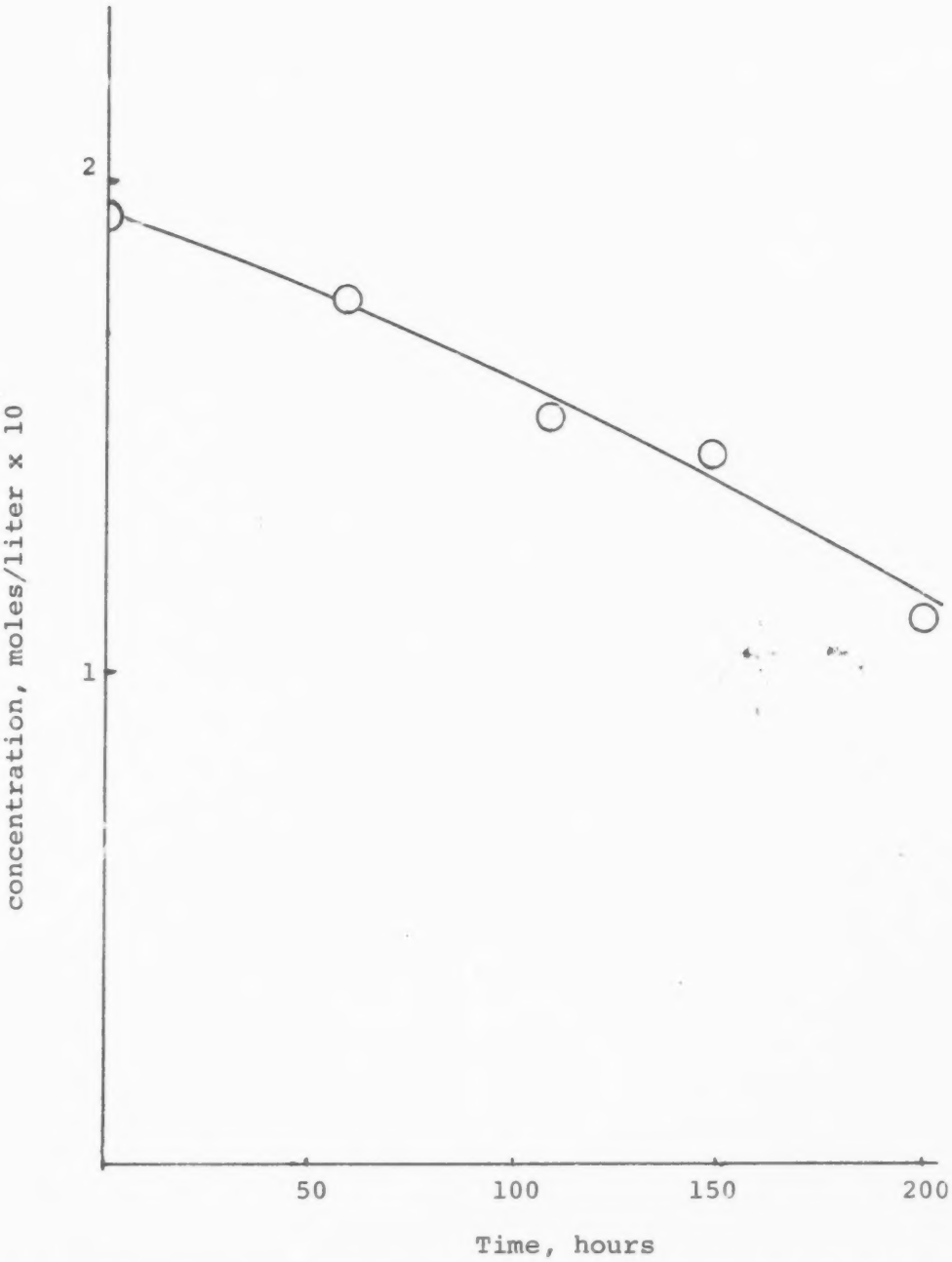


Figure 35 Rate of Photodegradation of Vat Blue 6 in Water at 50°C.

Figure 36 Rate of Photodegradation of Vat Green 1 in Water at 50°C.

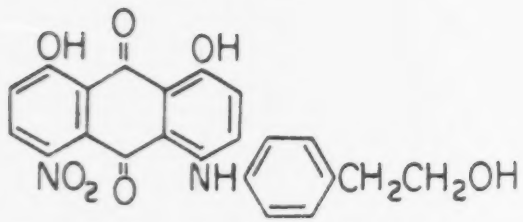
Because of their inherent light stability, this study of the vat dyes can give us an idea of the effect of physical changes on the fading of all pigmented types of dyes. The color changes that occurred with the vat dyes are mostly caused by changes in physical properties of the pigment dispersions. Obviously the dispersions are stable enough to color a waste stream for a long period of time. If biodegradable dispersing agents[20] are used in the commercially prepared dye, then the dispersion may be more easily destroyed in a biological waste treatment plant and some of the dye may be removed by adsorption on the sludge. Since the pigment is fairly inert the best method of removal is possibly by chemical coagulation.[21]

Disperse Dyes

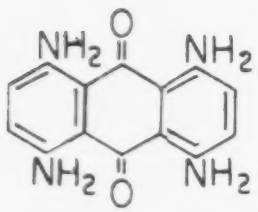
The disperse dyes were originally prepared for dyeing acetate fibers that were introduced to the textile markets after World War I.[22] These dyes are neutral organic molecules and have very low solubilities in water. Because of this they are ground with a dispersing agent in a similar manner to that used for vat dyes, and dispersed in water for use by the textile industry. These dyes are applied to polyester, nylon, acrylic and acetate fibers by batch operations and on continuous ranges. The batch operation uses a bath with a weight of approximately 30 times the fabric weight. The dye bath is heated to near boiling for one to three hours, then drained and the fabric rinsed. For some fibers, such as polyester, either carriers or pressure vessels are required to speed up the dyeing process. The carriers are organic compounds which swell the fiber, allowing the dye to penetrate. In the continuous process the dye solution is padded onto the fabric and dried and then heated at 200°C for one or two minutes. The dye penetrates the synthetic fiber at these high temperatures and excess dye is removed in a subsequent washing operation.

Because of the wide use of disperse dyes today, several of them were chosen for study--their structures are shown in Figures 37 and 38.

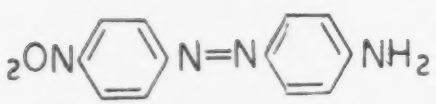
Disperse dyes, being in pigment form, are more resistant to light degradation than if they were dissolved in the water. This can be seen by the fading rate curves shown in Figures 39 to 46. The only dye that gave greater than 50% optical density decrease was Disperse Blue 3. The residue isolated from this dye solution after exposure could not be separated into identifiable fractions and no degradation products could be detected by mass spectral analyses.



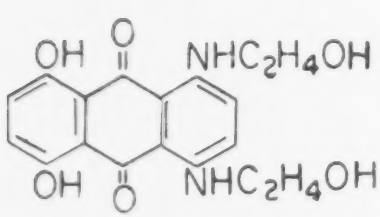
Disperse Blue 27 C.I. 60767



Disperse Blue 1 C.I. 64500

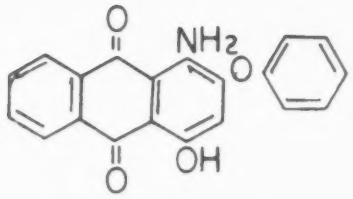


Disperse Orange 3 C.I. 11005

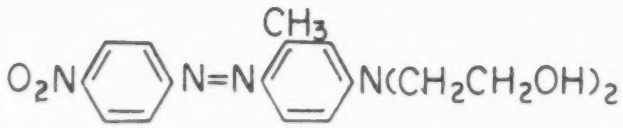


Disperse Blue 7 C.I. 62500

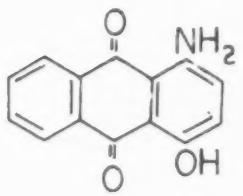
Figure 37 **Structures** of Disperse Dyes Studied



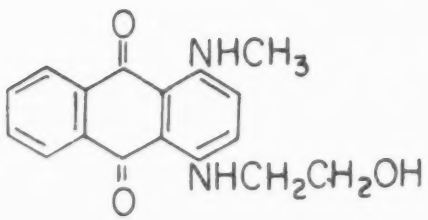
Disperse Red 60



Disperse Red 17 C.I. 11210



Disperse Red 15 C.I. 60710



Disperse Blue 3 C.I. 61505

Figure 38 Structures of Disperse Dyes Studied

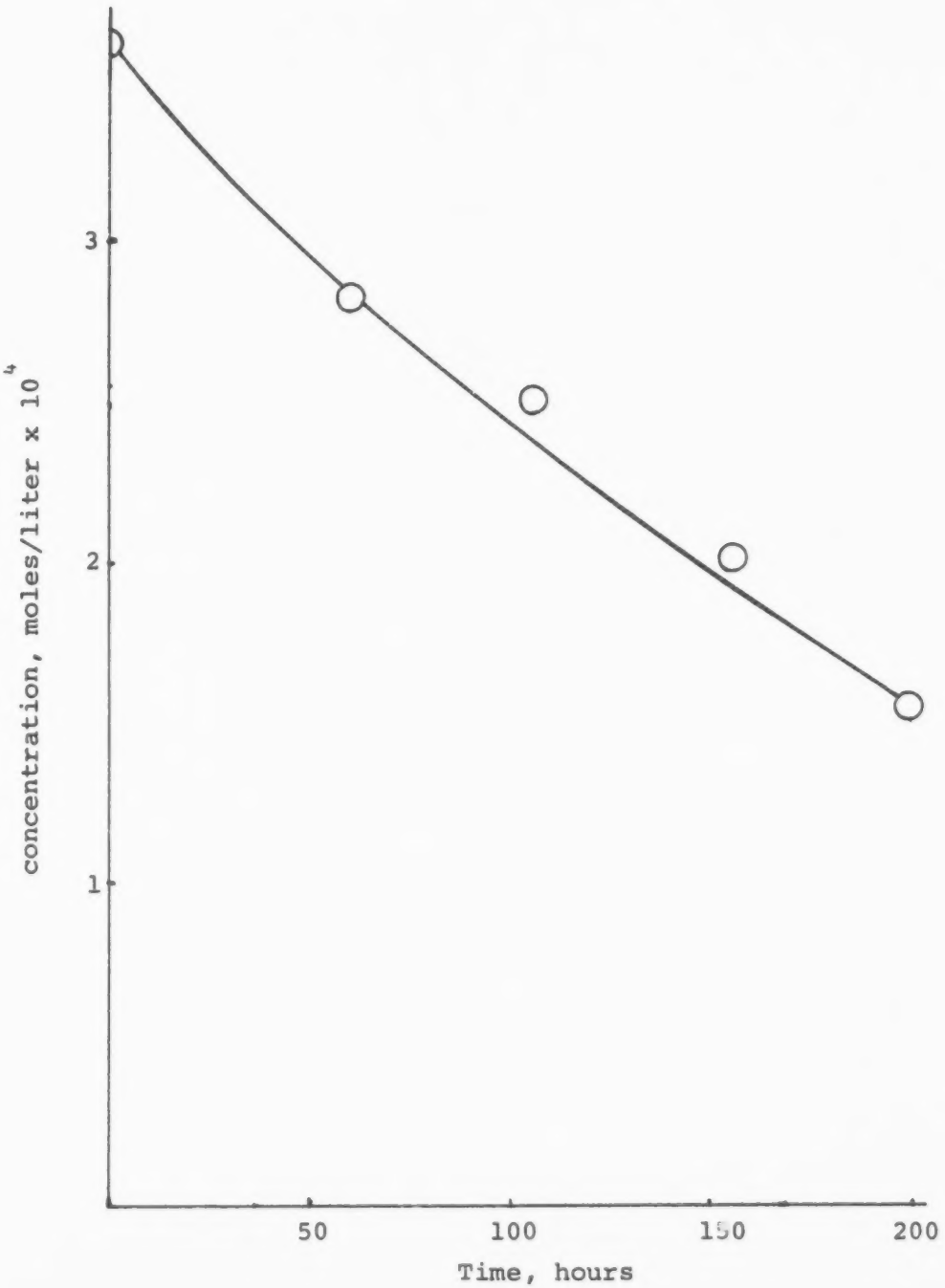


Figure 39 Rate of Photodegradation of Disperse Blue 3 in Water at 50°C.

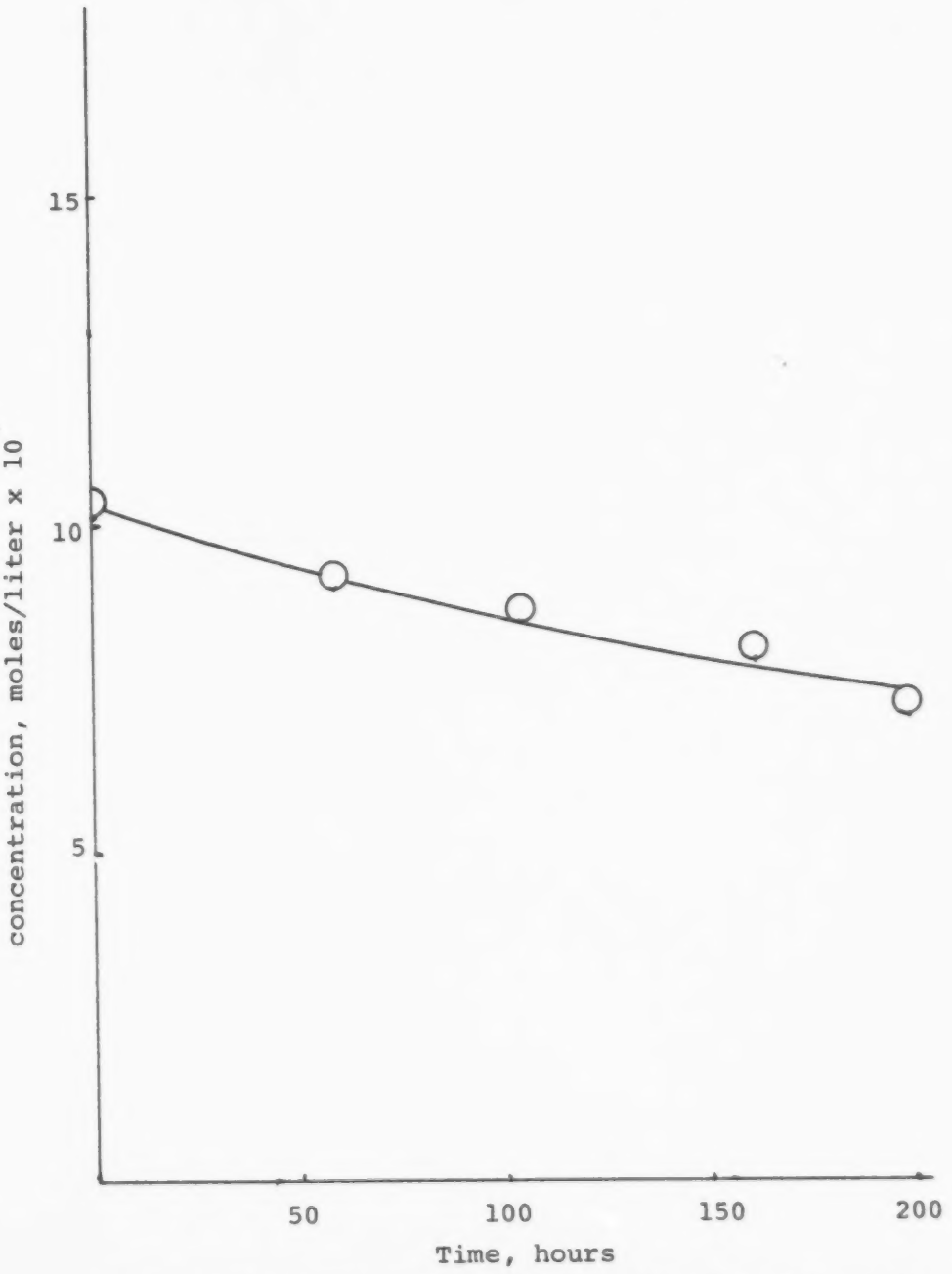


Figure 40 Rate of Photodegradation of Disperse Red 17 in Water at 50°C.

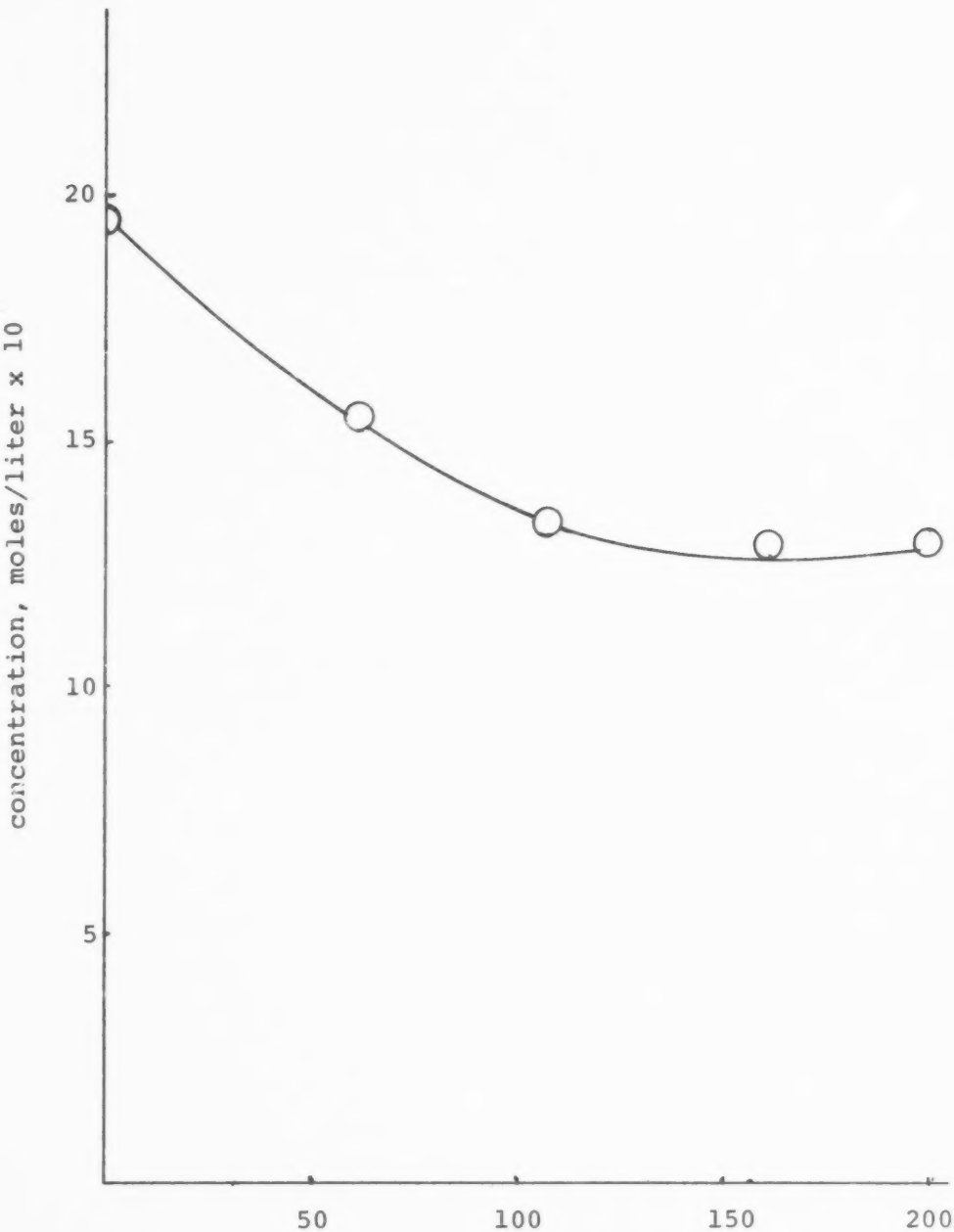


Figure 41 Rate of Photodegradation of Disperse Blue 1 in water at 50°C.

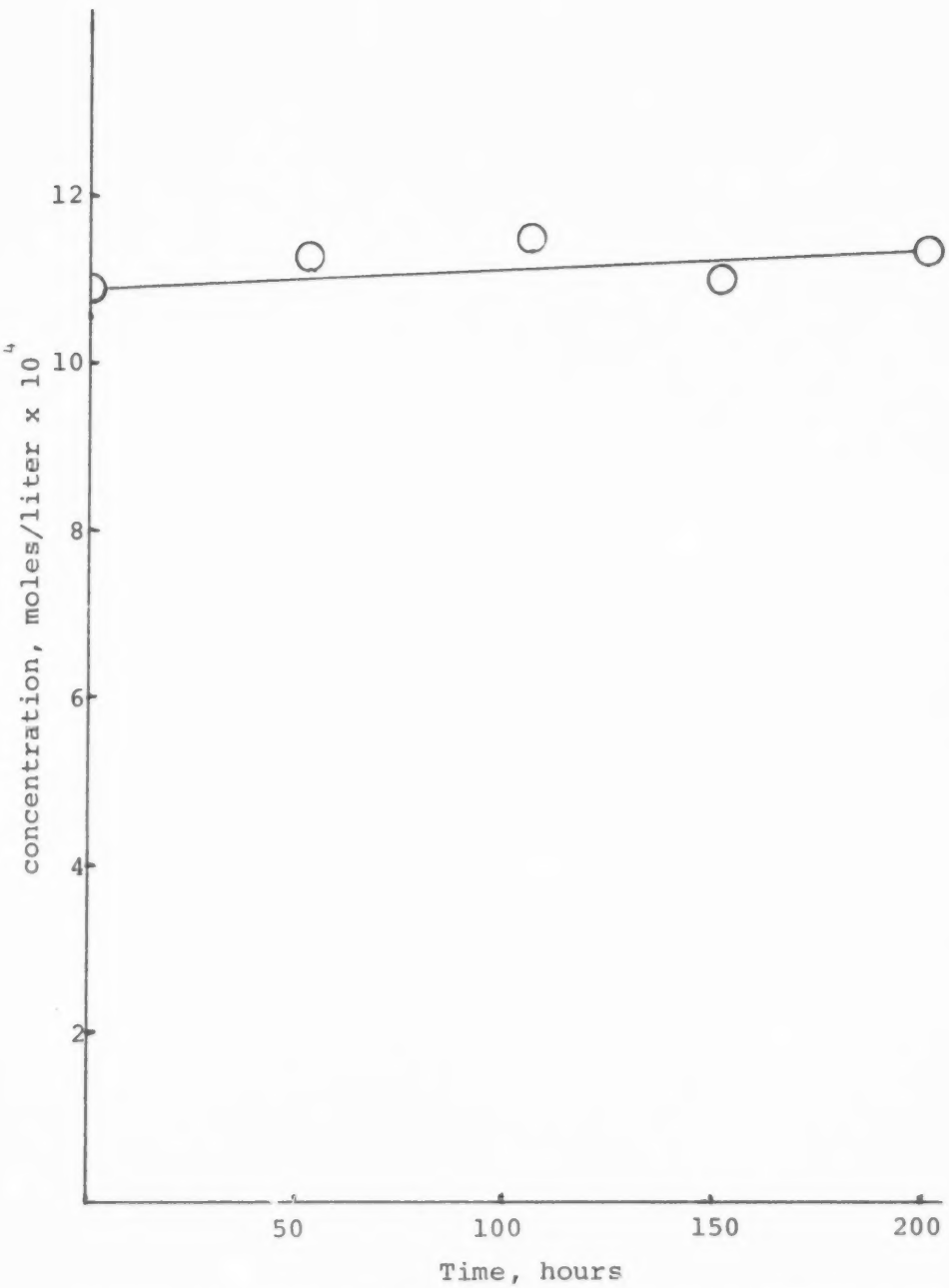


Figure 42 Rate of Photodegradation of Disperse Blue 27 in Water at 50 °C.

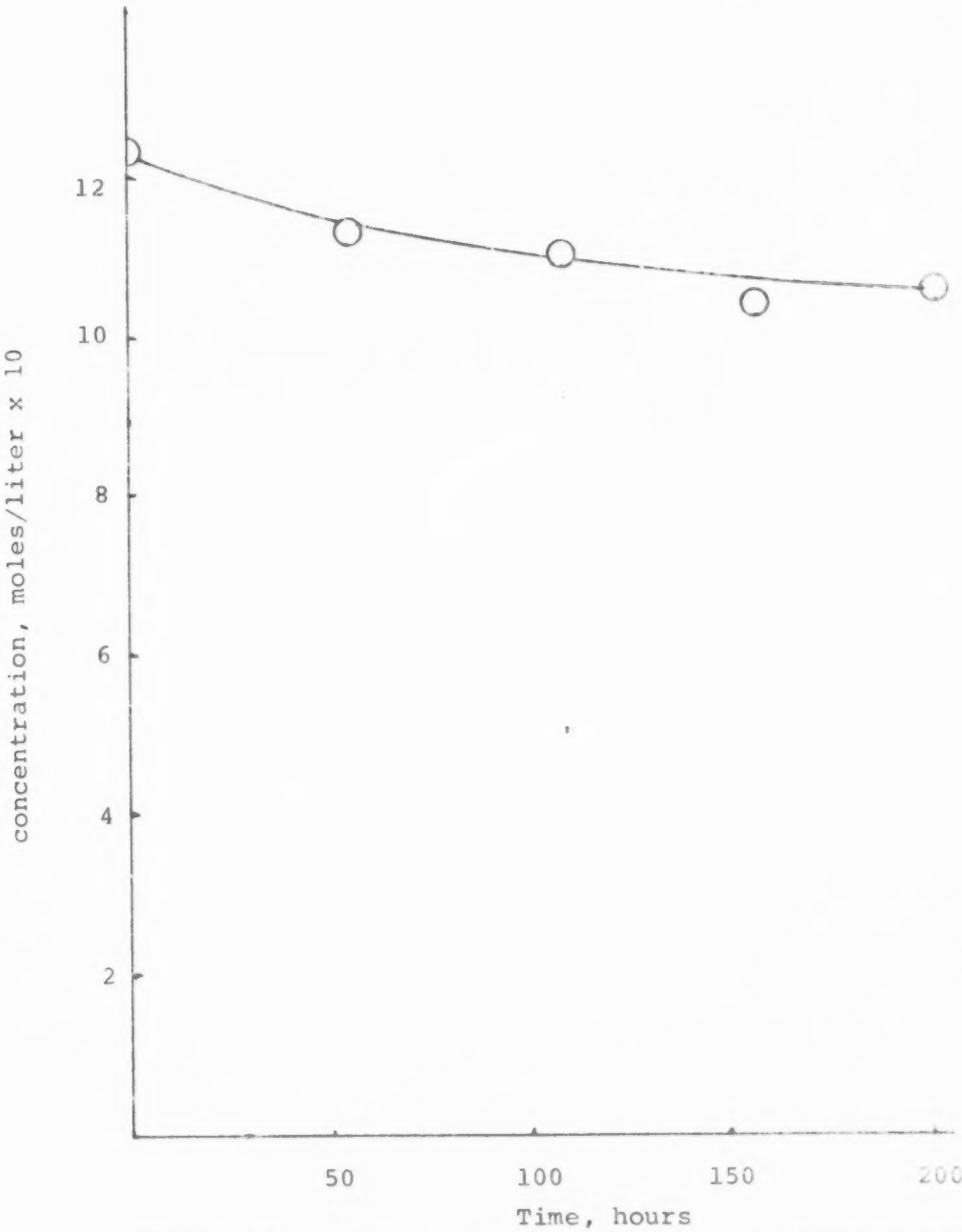


Figure 43 Rate of Photodegradation of Disperse Red 6 in Water at 50°C.

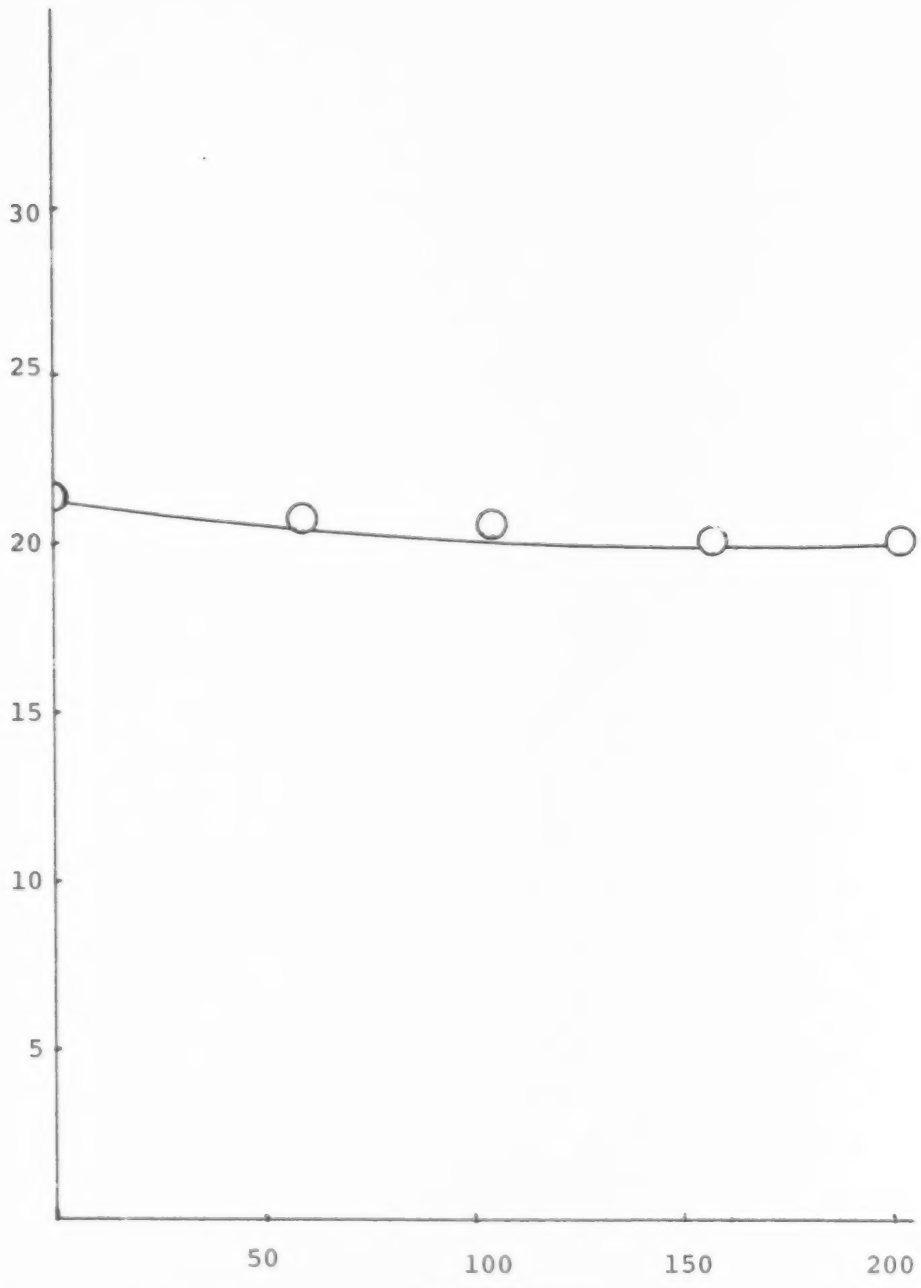


Figure 44 Rate of Photodegradation of Disperse Orange 3 in water at 50°C.

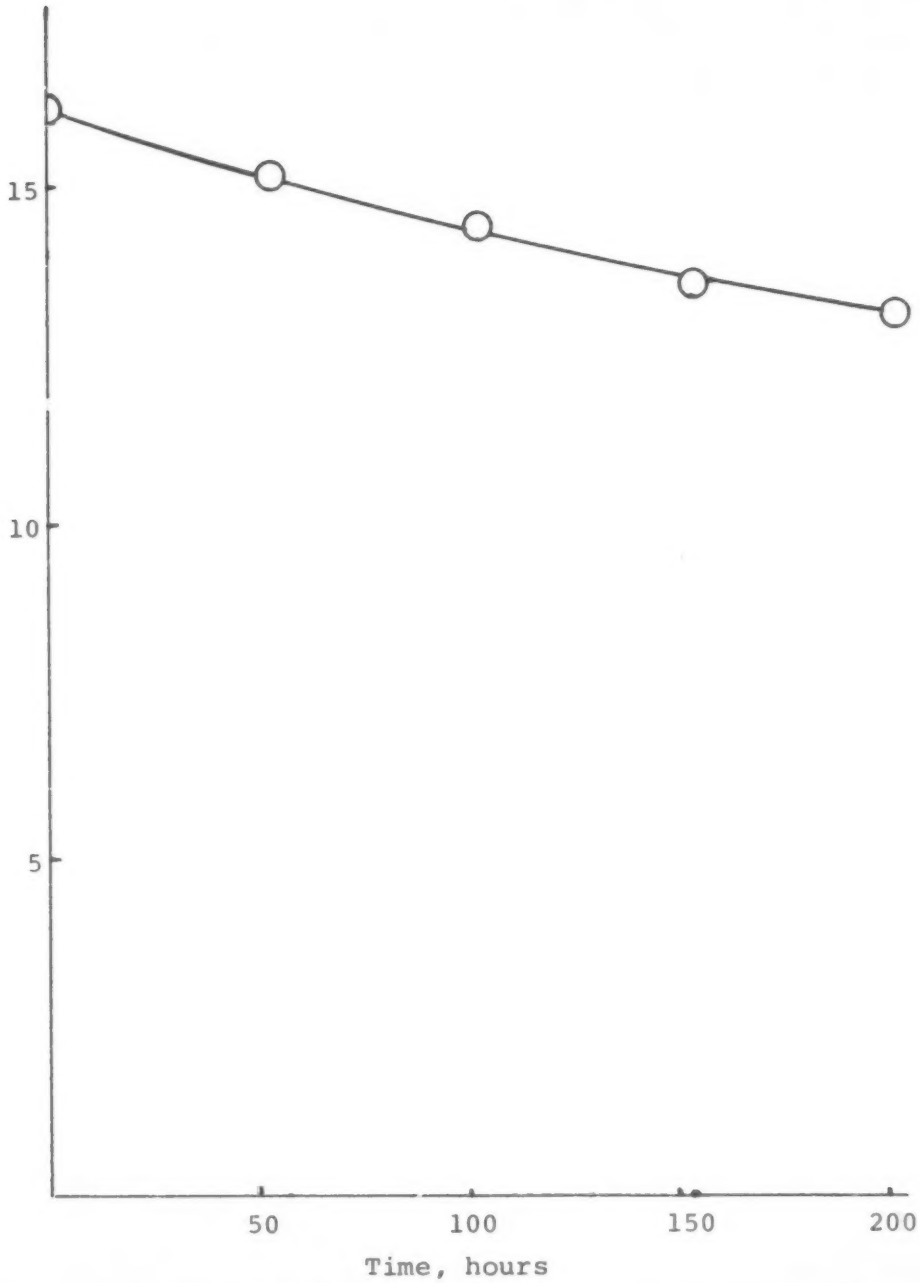


Figure 45 Rate of Photodegradation of Disperse Blue 7 in Water at 50°C.

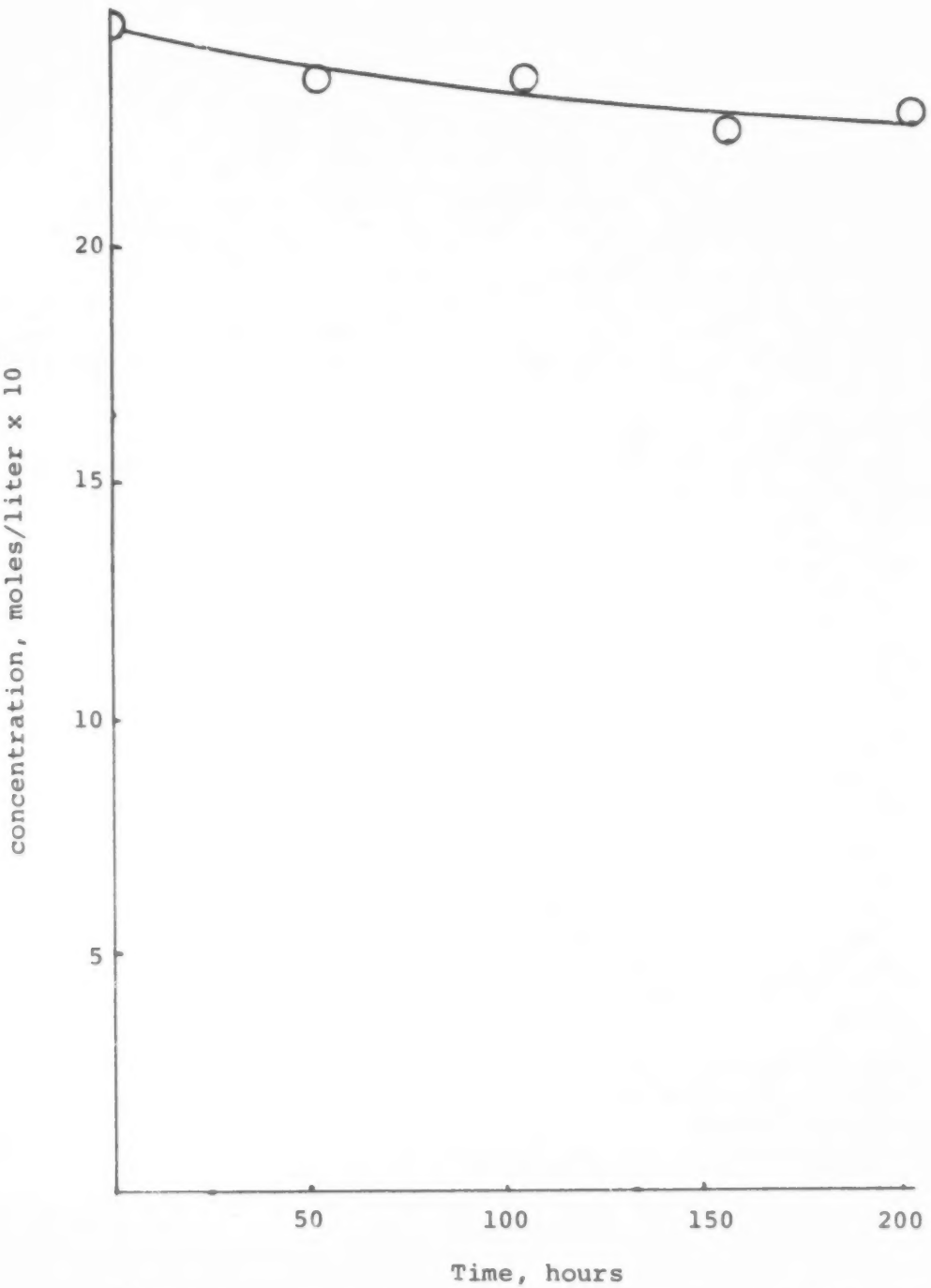


Figure 46 Rate of Photodegradation of Disperse Red 15 in Water at 50°C.

Since the disperse dyes are more soluble in water than the vat dyes[23] it was expected that they would degrade faster than the vat dyes when they were exposed to artificial light. This was not the case, as the data show. Disperse dyes are very resistant to degradation by the quantity of light that reaches natural streams and reservoirs.

Sulfur Dyes

Most sulfur dyes have complex structures that have not been completely characterized.[24] This is understandable when we consider that some of the first dyes of this class were synthesized from sawdust, bran or manure and sulfur. The newer dyes in this class utilize nitro aromatic systems as starting material. Their structures are less complex than the original dyes but still complex enough to prevent complete characterization.

These dyes are used exclusively on cellulose fibers and are applied from a bath containing sodium polysulfide and sodium hydroxide. The dye is soluble in this solution and can penetrate the fiber. The bath to fiber weight ratio is 30 to one and dyeing time is one to three hours. The dyes are also applied on a continuous range. The dye solution is padded onto the fabric and steamed. After the batch or continuous dyeing operation the dye is oxidized with air or sodium dichromate to the insoluble form which remains in the fiber.

Most of the sulfur dyes are mixtures containing several aromatic sulfur and nitrogen systems linked by a series of disulfide groups. These dyes thus have large molecular weights and very low water solubilities which no doubt account for their stability to light degradation. Sulfur dyes have good light and wash fastness on textile fibers so their stability in this study is expected. Because of the low extent of degradation of the sulfur dyes and their unknown structures no attempt was made to identify degradation products.

The degradation curves in Figures 47 to 50 show that these dyes could exist for a long period of time in a natural stream.

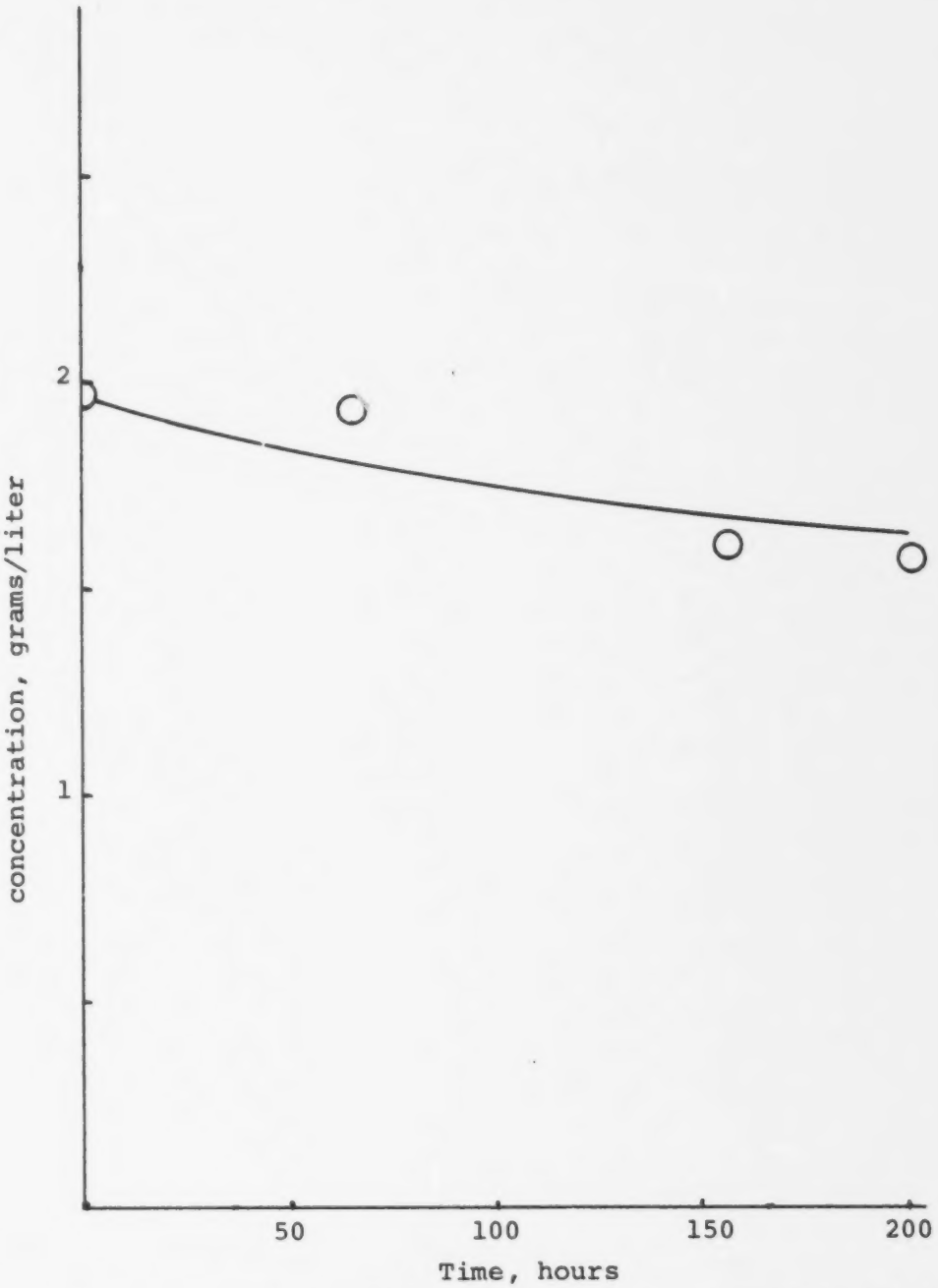


Figure 47 Rate of Photodegradation of Sulfur Red 5 in Water at 50 °C.

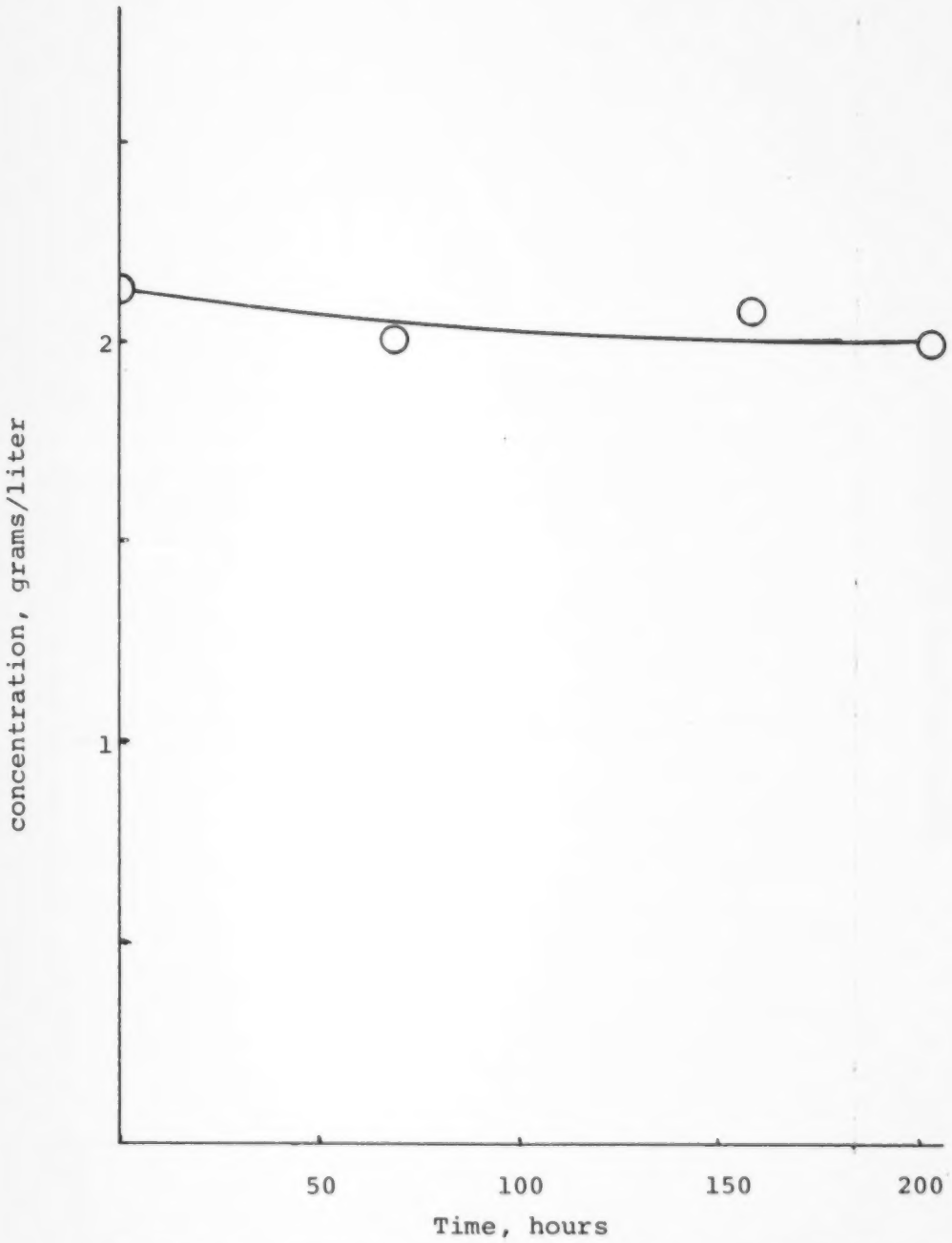


Figure 48 Rate of Photodegradation of Sulfur Blue 7 in Water at 50 °C.

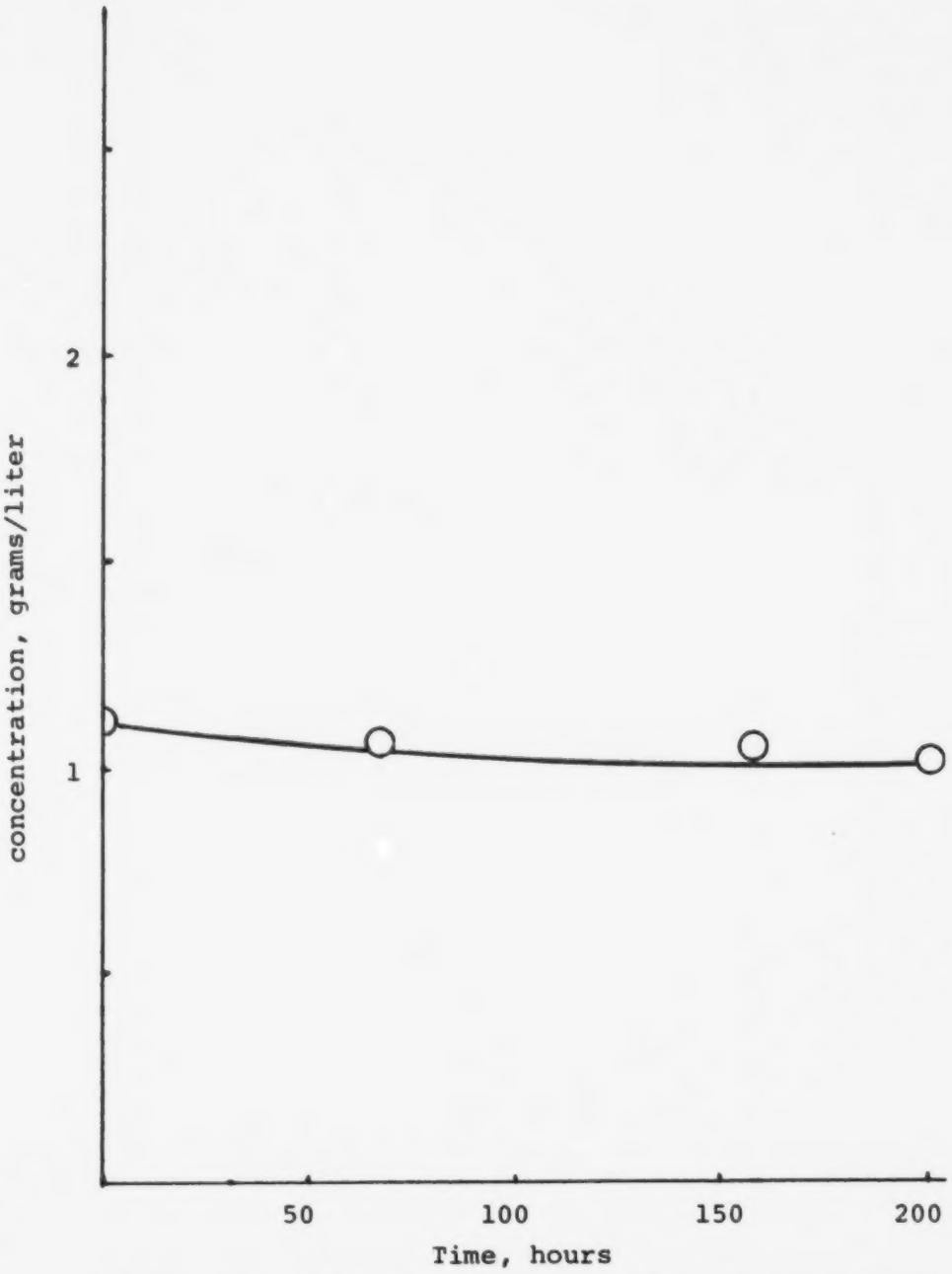


Figure 49 Rate of Photodegradation of Sulfur Blue 13 in Water at 50°C.

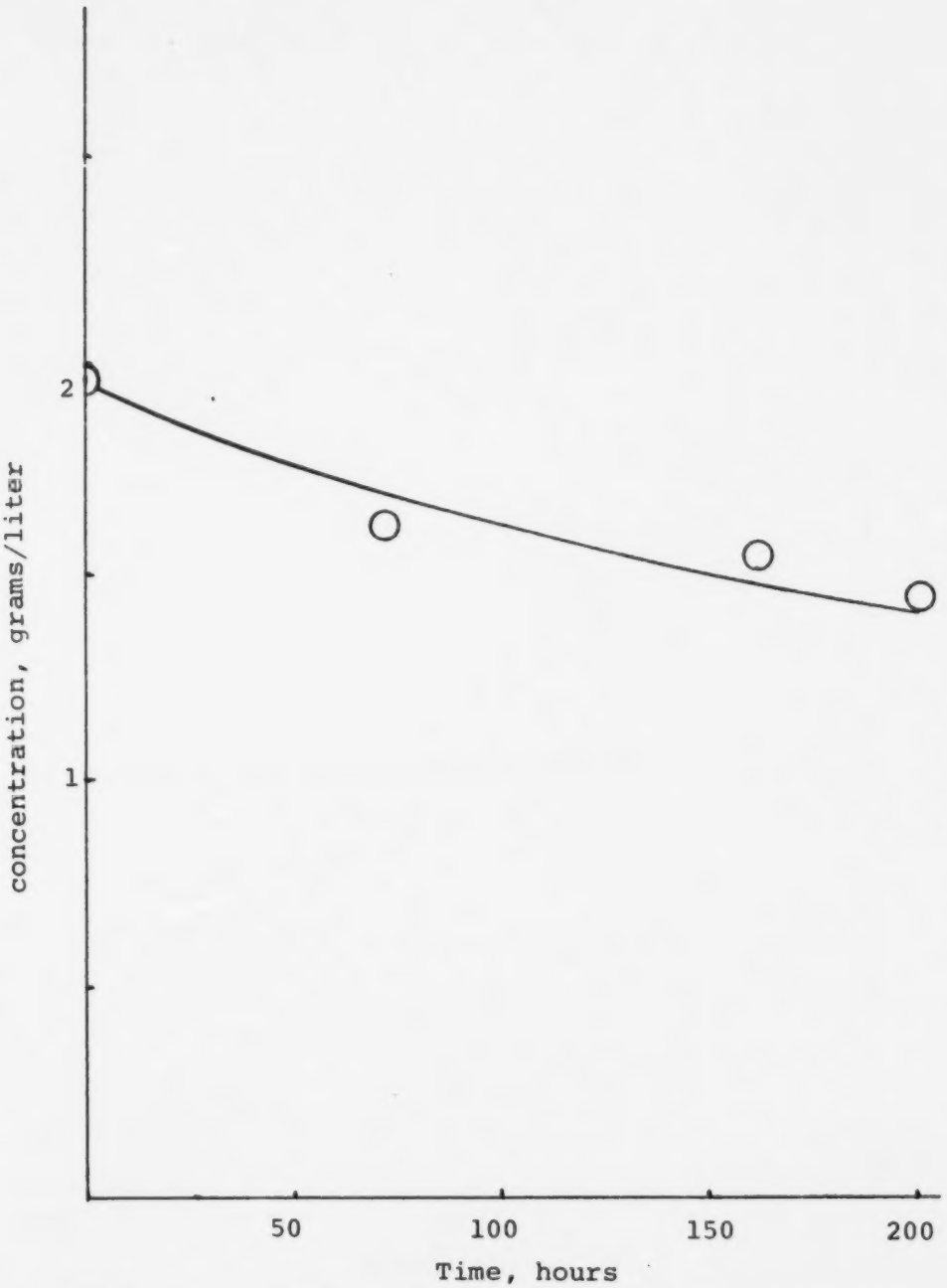


Figure 50 Rate of Photodegradation of Sulfur Black 1 in Water at 50°C.

SECTION V

ACKNOWLEDGEMENTS

The investigator expresses his appreciation to Scott B. Speares and Marshall White, Jr., who assisted in this work. Thanks are also given to Dr. Arthur W. Garrison of the Southeast Water Laboratory, Athens, Georgia, EPA, for his assistance with the analytical work and helpful discussions over the course of the study. Finally, appreciation is expressed for the cooperation and financial support of the Office of Research and Monitoring of the Environmental Protection Agency.

SECTION VI

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